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BRICK G. POWER
TRASK, BRITT & ROSSA LAW OFFICES
P.O. BOX 2550
SALT LAKE CITY, UT 84110

EXAMINER	
PIERCE, WILLIAM M	
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Please find below and/or attached an Office communication concerning this application or proceeding.

PTO-90C (Rev. 07-01)

(5) Summary of Invention

The summary of invention contained in the brief is correct.

(6) Issues

The appellant's statement of the issues in the brief is correct.

(7) Grouping of Claims

Appellant's brief includes a statement that claims 1,10, 20 and 27 do not stand or fall together and provides reasons as set forth in 37 CFR 1.192(c)(7) and (c)(8).

(8) Claims Appealed

The copy of the appealed claims contained in the Appendix to the brief is correct.

(9) Prior Art of Record

4,722,815	Shibanai	2/1988
4,293,602	Coffey et al.	10/1981
4,762,493	Anderson	8/1988

(10) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

Claims 1-3, 5, 7, 8, 10-27, 29 and 31 are rejected under 35 U.S.C. 103(a) as being unpatentable over what is old and well known in bowling balls in view of Shibanai.

As to claims 1-3, 5, 7, 10-19, 20-27, 29 and 31, bowling balls of nonporous polymeric thermosetting resin is old and well known. This is admitted old at the bottom of pg. 2 of Appellant's specification. Lacking in bowling balls is the use of a fragrance. However, perfumed polymers intended for the purpose of making plastic articles with a fragrance are also well known. Shibanai teaches compounds to be included in synthetic resin products in order to enhance their smell. While there is no direct teaching of using his compound in a bowling ball, it has been held that, in evaluating a reference, it is proper to take into account not only the specific teaching of the reference(s) but also the inferences which one skilled in the art would reasonably be expected to draw therefrom. In re Preda, 401 F.2d 825, 826, 159 USPQ 342, 344 (CCPA 1968). Additionally, one must observe that an artisan must be presumed to know something about the art apart from what the references disclose (see In re Jacoby, 309 F.2d, 513, 516, 135 USPQ 317, 319 (CCPA 1962). In line with this, one skilled in the art would clearly have found it obvious to have applied perfumed compounds, such as Shibanai's in order to make a bowling ball smell better. Where the claims call

for a two-part resin and the fragrance being dissolved therein, Shibanai directly teaches that "it is also possible to mix perfume...with a synthetic resin compound followed by molding" (col. 1, ln. 26) but that this "direct addition of perfume...to synthetic resin compound is not as effective as it seems" (col. 1, 35). Hence Shibanai goes on to teach an improved more effective method of adding fragrance to a product that includes forming an inclusion compound consisting of perfume included in cyclodextrin. While Shibanai does not detail the old and known methods of "mixing perfume" and "direct addition of perfume" that is at least partially dissolved within the resin, such are considered old when one further considers Coffey et al. as an example. Coffey teaches that it is an old expedient and would have been obvious to mix fragrances to two part resins in the forming of a fragrances polymer product. Edwards and Wilbert, are further examples of direct mixing of fragrances with a polyurethane prior to molding. The art is replete with the successful addition of fragrance to two part polymer products. The motivation is simply to "impart to other polymeric products pleasant odors" (Wilbert, col.1, ln. 57).

The amount of fragrance as called for in claim 8 is considered and obvious matter of choice depending upon how strong of a smell is desired.

Claims 9, 32 and 33 are rejected under 35 U.S.C. 103(a) as being unpatentable over bowling balls in view of Shibanai and further in view of Anderson.

Applying a pigment to polymer resin products to give them color is old and well known. Anderson teaches that it is old to apply a color that correlates to a fragrance in a product. To have done so with a bowling ball would have been obvious to one skilled in the art for the novelty.

Applicant's arguments with respect to claims 1-33 have been considered but are moot in view of the new ground(s) of rejection.

(11) Response to Argument

SECTION A and B

Appellants remarks are noted but no response is deemed necessary since they merely set forth his interpretation of controlling case law and the applied art.

SECTION C

In the first office action, the applied art and the rejection set forth by the examiner made it clear that adding fragrance in general to plastics is old and well known. Shinbanai, the primary reference, shows a plastics additive

containing perfumes and gives numerous examples pertaining to its use in thermoplastics. In response to this first office action, appellant added the term "two-part resin" to the claims.

First, one must look at the terms used in the claims in order to determine their scope. As such it is necessary to review the specification order to establish whether the meaning of those terms and phrases given by the applicant in the context of the application should be accorded any meaning different from the usual and customary meaning of the claim terms. Upon doing such, it can be concluded that any plastic made up of two components can be considered a "two-part resin". Supporting this conclusion can be found in the specification where it notes that "conventionally, bowling balls have been formed from machinable, thermosetting plastic materials." (pg. 2, [0002]). Paragraph [0004] of pg. 2 discusses reactive polymers that require the addition of a catalyst for polymerization. Nowhere in the specification does appellant consider or define polymers requiring a catalyst (such as the ones discussed in paragraph [0004]) to be defined as "two-part resins". Compounded by the fact that many known thermosetting resins contain other numerous components such as fillers, promoters, inhibitors and reactive components such as Isocyanates (used commonly to produce polyurethane foams or cellular rubber). To the extent that known thermosetting resins can be "two-part" based upon its composition including more than one component in its making, there is no distinction between the "thermosetting" resins to which Shibanai discloses adding his fragrance material and one, such as an epoxy resin, requiring a catalyst. For example Shibanai is considered to disclose a "two-part" resin of a "synthetic resin compound and glycitol(s)" (col. 17, ln. 51).

Lastly, even if one were to recognize the term of "two-part resin" to mean a polymer of the type requiring a resin. These resins are still "thermosetting resins" per se. However, the heat required for polymerization is provided by a chemical reaction (. Note pg. 4 of the Handbook of Reinforced Plastics that list "epoxy resins" as a "thermosetting resin". On pg. 71, ln. 16, these epoxy resins are of the type requiring "hardeners or curing agent" that react to polymerize the resins. As can be clearly seen by the Handbook, one skilled in the art of plastics fully recognizes the uses, properties and manufacturing practices for making products and selecting a material for its intended purpose.

Appellant's initial remarks at the top of pg. 11 of the Brief alleging that Shinbanai are "limited to use of a thermoplastic resin" are moot in view of the ordinary level of skill as discussed above. In the first point above, it is shown that thermosetting resins, such as those in Shinbanai, can be considered to be "two-part" resins within the scope of the claims since they can contain fillers and other additives. In the last portion of the discussion above, it is shown that there is no distinction in the art between "one-part" and "two-part" resins as implied by appellant. Even

though a polymer requires a catalyst for polymerization (as opposed to external heat) as in the case of an epoxy resin, such are still considered to be "thermosetting resins".

Claims 11-13, 18 and 19, including polyol in the method of manufacturing of a bowling ball is old. This is admitted by appellant on his specification, paragraph [0004]. To further assist the Board in making its determination and to appropriately determine what is known in the art, the examiner has appended two websites that discuss the uses of Polyol with respect to polyurethanes. Note http://www.kosa.com/poly/specprod.htm and http://polyol.synair.com/About%20Polyols.htm, copies of which are appended to this examiners answer.

As to claim 20, skill has to be presumed on the part of a person practicing the invention of Shinbanai. Known is that once the catalyst is added to polyol, there a "working time" for the resin is set. Mixing the fragrance into the polyol prior to the catalyst does nothing more than what would be obvious to the skilled artisan. Further, it is clear that the fragrance could be added to the polyol after the addition of the catalyst. However, it would need to be done such that it could be uniformly mixed and molded before polymerization were to begin.

As to claims 20 and 21-26, the removal of gas "trapped" in a polymer mixture is old and inherent in the art of plastics. Failure to do so results in an inferior final product made by the visibility of "bubbles" that art trapped after the product has fully cured. Surely applicant is not the inventor of removing trapped air or gas known throughout the plastics industry.

As to claim 21, Webster's New World Dictionary defines "dissolve" as "to merge with a liquid". Shinbanai clearly teaches a fragrance that is to be "merged" with a liquid polymer. As such, claim 21 is considered fairly taught.

As set forth above, a catalyst is well known as being used with polyols to cause polymerization. The use of a catalyst as called for in claim 23 is not new to the art of plastics.\

The use of isocyantes as called for by claim24 is old. The Boards attention is drawn to pg. 5 of the Handbook. As mentioned previously in the Answer, they are mostly known for having a "foaming" affect on plastic compositions.

Claims 27, 29 and 31 amount to a mere allegation of patentability base on their dependency of claim 1. Since claim 1 has been shown above not to be patentable, these claims too are considered not patentable. Neither Shinbanai nor Coffey "teach away" from the instant invention as appellant states at the top of pg. 13. Well known is that the teaching of Shinbanai and Coffey are to be read in light of what is known in the prior art and for what they "would suggest". As noted by Shinbanai, the direct addition of certain addatives (for example insecticides) are "so volatile, liable to denature and unstable to heat that it is difficult to practice to mold a mixture" (col. 1, ln. 40). He suggest the it is clearly possible. However, Shinbanai's invention makes it easier and is an improvement upon

traditional methods of directly adding such substances to a synthetic resin product. Further note that an artisan is not compelled to blindly follow the teaching of one prior art reference over another without the exercise of independent judgement. *Lear Siegler, Inc. v. Aeroquip Corp., 733 F.2d 881, 889, 221 USPQ 1025, 1032 (Fed. Cir. 1984).* First, one skilled in the art would not consider the teachings of Shinbanai to be restricted to thermoplastics or thermoset resins. Second, as stated above and as taught by Handbook, two-part resins such as "epoxy" are known to be classified as a thermoplastic.

One wishing to enhance the "smell" of a bowling ball would clearly consider what others before them have done to make other plastic product smell better. As such both Shinbanai and Coffey are directly analogous to the problem at hand.

The discussion of "hook" has little to do with whether or not one would be motivated to add fragrance to a plastic product. True bowling ball designers a greatly concerned with the surface properties of a ball that affects its performance. However, there are no suggestions that the addition of an inert substance or filler would change the performance of the ball. Nor is there any evidence of record that appellant has overcome any particular performance problems faced with adding fragrances to bowling balls. Lastly, it is to be noted that the design of bowling balls has been mostly a trial and error process. A ball of a particular compound is made and then its performance is noted. How a ball performs and "hooks" depends upon the preference and style of the bowler. The word "motivation" or a word similar to "motivation" does not appear in 35 U.S.C. § 103(a). While a finding of "motivation" supported by substantial evidence probably will support combining teachings of different prior art references to establish a prima facie obviousness case, it is not always necessary. For example, where a claimed apparatus requiring Phillips head screws differs from a prior art apparatus describing the use of flathead screws, it might be hard to find motivation to substitute flathead screws with Phillips head screws to arrive at the claimed invention. However, the prior art would make it more than clear that Phillips head screws and flathead screws are viable alternatives serving the same purpose. Hence, the prior art would "suggest" substitution of flathead screws for Phillips head screws albeit the prior art might not "motivate" use of Phillips head screws in place of flathead screws. What must be established to sustain an obviousness rejection is a legally sufficient rationale as to why the claimed subject matter, as a whole, would have been obvious notwithstanding a difference between claimed subject matter and a reference which is prior art under 35 U.S.C. § 102. Once a difference is found to exist, then the examiner must articulate a legally sufficient rationale in

support of a §103(a) rejection. The legally sufficient rationale may be supported by a reason, suggestion, teaching or motivation in the prior art which would have rendered obvious the claimed subject within the meaning of § 103(a). *In re Dance*, 160 F.3d 1339, 1343, 48 USPQ2d 1635, 1637(Fed. Cir. 1998) (there must be some teaching, suggestion or motivation in the prior art to make the specific combination that was made by the applicant); *In re Gartside*, 203 F.3d 1305, 1319, 53 USPQ2d 1769, 1778(Fed. Cir. 2000) (the best defense against the subtle but powerful attraction of a hindsight-based obviousness analysis is rigorous application of the requirement for a teaching or motivation to combine prior art references); *Pro-Mold and Tool Co. v. Great Lakes Plastics Inc.* 75 F.3d 1568, 1573, 37 USPQ2d 1626, 1629(Fed. Cir. 1996) ("there must be a reason, suggestion, or motivation *** to combine [the teachings of] *** references ***"). Hence, whether bowling balls "hook" or not, does nothing to show insufficient motivation to combine the references where the prior art teaches it is desirable to add fragrance to polymer products.

As to Sinbanai, Coffey and Anderson, Anderson was added to teach the adding color pigments that "match" the "smell". Such a connection between sight and smell is well known in the art. As such to have a red bowling ball that smells of strawberries is not considered a patentable advance as fairly taught by the applied art.

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,

WILLIAM M. PIERCE
PRIMARY EXAMINER

wp
April 7, 2003

Conferees;
Paul Sewell

Steven Wong
Primary Examiner

BRICK G. POWER
TRASK, BRITT & ROSSA LAW OFFICES
P.O. BOX 2550
SALT LAKE CITY, UT 84110

KoSa

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Specialty Products

Terate® Polyols

- Aromatic Polyols From the Complete Polyester Resource
- A Leader in the Industry
- Our Growth
- Product Advantages
- Standard Product Information
- Guidelines for Storage and Handling
- Availability and Reliability
- Customer Service, Sales, and Technical Information

Aromatic Polyols From the Complete Polyester Resource

KoSa offers a diverse line of Terate® aromatic polyester polyols for use in polyurethanes. Our polyols are available in a wide variety of equivalent weights and properties to allow for formulation flexibility. Processes using Terate polyols achieve the rigorous physical and flammability properties required in many rigid polyurethane (PUR) and polyisocyanurate (PIR) foams. The high aromaticity of Terate polyols, along with their low cost, makes them extremely desirable for many applications.

In flammability tests, PIR and PUR foams containing Terate polyols result in excellent char formation with minimal shrinkage and high weight retention.* In many formulations, the unique aromatic backbone of Terate polyols reduces or eliminates the need for expensive flame retardants.

* As demonstrated in ASTM E-84 and Factory Mutual calorimeter testing with HCFC 141b, pentane, and partially water-blown foams.

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A Leader in the Industry

New product development, experienced technical service and computerized process control make KoSa's Terate polyols an industry leader. Market demands, such as blowing agent replacement and increased polyester polyol ratios, create challenges for foam formulators. KoSa's Terate professionals work proactively with customers and co-suppliers to develop optimal Terate-based PUR and PIR formulations.

As the world's largest producer of dimethyl terephthalate (DMT) - the raw material source for Terate Polyols - we can ensure that our customers receive an uninterrupted supply of consistent, high-quality products.

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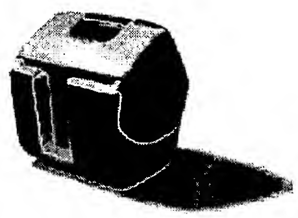
Our Growth



Our Terate polyols were first produced in 1974 by Hercules at its Wilmington, NC, USA, site. Since 1989 when the current Terate team was formed, production has increased eight-fold and continues to increase at our newest production facility in Vlissingen, Netherlands.

Although our name has changed over the years - from Hercules to Cape Industries to Hoechst Celanese, and now to KoSa - our commitment to polyester and new applications for Terate polyols has remained constant. With continued enhancements of our products, KoSa provides the best polyester polyols for many applications in the urethane industry.

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Product Advantages

KoSa Terate polyols are ultimately designed to give our customers greater flexibility and control with their products. Additionally, our experience and capabilities provide customers with:

- Industry-leading technical service in formulation and production
- Reliable supply of internal raw material available
- Computerized quality process control
- Excellent flame-resistance results
- Multi-property product line
- Consistent quality products
- Blowing agent compatibility
- Cost advantage over polyethers
- High aromatic content
- Good flow properties
- Uniform reactivity

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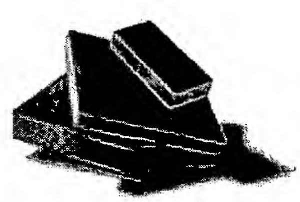
Standard Product Information



Terate polyols are available in the following basic series featuring a variety of options in color, viscosity, acidity, processability, hydroxyl value and functionality. This list includes typical property ranges for each series. Please refer to data sheets available from your KoSa representative for actual product specifications and applications.

Value Range

Product Series	Hydroxyl Value (mgKOH/g)	Viscosity (cps@25°C)	Functionality	Acidity (mgKOH/g)	Average Equivalent Weight	Specific Gravity (g/ml)
Terate 2000	280 - 335	3,000 - 22,000	2.3	0.5 - 4.0	181	1.2
	The original Terate polyol with high functionality use in bunstock, panel, pour-in-place, spray and foundry systems. Available in lower acid numbers.					
Terate 2500	225 - 275	2,700 - 7,700	2.0	0.4 - 2.0	238	1.2
	A polyol series with excellent flammability in polyisocyanurate foams with minimal shrinkage and high weight retention. In many formulations, the unique aromatic backbone reduces or eliminates expensive flame retardants. Used in laminate, panel, pour-in-place and spray systems.					
Terate 3000*	230 - 255	2750 - 7,500	2.0	0.6 - 1.2	230	1.2
	A series of polyols developed for hydrocarbon blown foam applications with improved characteristics over the 2500 series.					
Terate 4000*	295 - 350	1,500 - 6,000	2.0 - 2.2	0.2 - 1.5	175	1.2
	An amber polyol series used in appliance systems and for other low viscosity requirements. Similar to our 2000 serires, but with reduced viscosity.					
Phenrez®*	50 - 100	700 - 10,000	-	2.0 - 10	-	1.13
	A dark, high-polar, liquid aromatic polyester resin used in foundries producing furan no-bake (FNB) resin systems.					

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*Please check with a KoSa representative about availability in your area.

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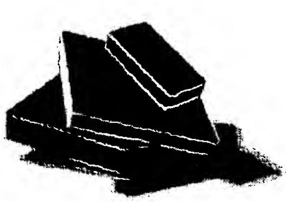
Guidelines for Storage and Handling



Terate polyols can be stored and handled in tanks made of carbon steel,stainless steel, fiberglass or other conventional construction materials. Storage temperatures should be kept below 60°C (140°F) to maintain product integrity. Storage vessels and process tanks also should be protected with dry air [minimum 4.4°C (-40°F bulb)] or nitrogen to prevent uptake of atmospheric moisture. Please see the MSDS for specific details on handling individual products.

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Availability and Reliability

Terate polyols are shipped worldwide in lined, closed-head drums, tank trucks, and tank cars from KoSa's US and European facilities. Samples are available upon request. Our Terate polyol team will be glad to arrange a delivery system to best meet your needs.

Terate® and Phenrez® are registered trademarks of KoSa.

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SYNAIR CORPORATION

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About Polyols

Synair Corporation
Post Office Box 5269
2003 Amnicola Highway
Chattanooga, TN 37406
USA

(423) 697-0400 main
(423) 697-0443 fax

Polyurethanes are based the exothermic reaction of polyisocyanates and polyol molecules. Many different kinds of polyurethane materials are produced from a few types of isocyanates and a range of polyols with different functionality and molecular weights. Some of the diversity of functionality depends on whether the polyols are based on polyether or polyesters. Condensation based polyols are used primarily in the construction and building industries for efficient insulation in roofs, wall cavities, and flooring. Polyether polyols are used in a wide range of rigid and flexible polyurethane applications, including energy saving refrigeration insulation, industrial sealants, cushion foam, and construction and building materials.

Polyether polyols contain the repeating ether linkage –R–O–R– and have two or more hydroxyl groups as terminal functional groups. They are manufactured commercially by the catalyzed addition of epoxies (cyclic ethers) to an initiator. The most important of the cyclic ethers by far are propylene oxide and ethylene oxide, with smaller quantities of butylenes oxide also being consumed. These oxides react with active hydrogen-containing compounds (called initiators), such as water, glycols, polyols and amines; thus, a wide variety of compositions of varying structures, chain lengths and molecular weights is theoretically possible. By selecting the proper oxide (or oxides), initiator, and reaction conditions and catalysts, it is possible to synthesize a series of polyether polyols that range from low-molecular-weight polyglycols to high-molecular-weight resins. Most polyether polyols are produced for polyurethane applications; however, other end uses range from synthetic lubricants and functional fluids to surface-active agents.

Since these polymers contain repeating alkylene oxide units, they are often referred to as polyalkylene glycols or polyglycols. The terms *polyglycol* and *polyether polyol* are used interchangeably; however, the term *polyalkylene glycol* is used when these types of products are used in nonpolyurethane applications. The physical properties of the polyols are influenced primarily by the functionality of the initiator molecules and by the type and quantity of alkylene oxide and hydroxyl groups present in the polyol. In general, the functionality of the polyether is carried over from the functionality of the initiator used.

Two types of urethane polyols are prepared from propylene oxide. The first type results from the reaction of propylene oxide with compounds having an active hydrogen (usually donated by a hydroxyl or amine group); these polymers are typically atactic. Polymers of the second type are essentially those of propylene oxide itself and are commonly called polypropylene oxide or polypropylene glycol; they are in most cases isotactic. Mixtures of atactic and isotactic polymers may also occur.

The following table lists most of the major commercially available polyether polyol types used in urethane manufacture, plus the initiators and cyclic ethers (oxides) used in their preparation:

Selected Commercial Polyether Polyols and Reactants

Product	Initiator	Cyclic Ether
Difunctional		
Polypropylene Glycol (PPG)	Water or propylene glycol	Propylene oxide
Polyethylene Glycol (PEG)	Water or ethylene glycol	Ethylene oxide
Polyoxypropylene-Polyoxy-ethylene Block Copolymer	Water, propylene glycol or glycerin *	Propylene oxide and ethylene oxide
Polytetramethylene Ether Glycol (PTMEG)	Water	Tetrahydrofuran
Aromatic Diol	Bisphenol A	Propylene oxide or ethylene oxide
Amine Adducts	Primary monoamines **	Propylene oxide or ethylene oxide
Trifunctional		
Glycerin Adduct	Glycerin	Propylene oxide
Trimethylolpropane Adduct	Trimethylolpropane	Propylene oxide
Trimethylolethane Adduct	Trimethylolethane	Propylene oxide
Tetrafunctional		
Pentaerythritol Adduct	Pentaerythritol	Propylene oxide
Ethylenediamine Adduct	Ethylenediamine	Propylene oxide
Phenolic Resin Adduct	Phenolic resin	Propylene oxide
Methyl Glucoside Adduct	Methyl Glucoside	Propylene oxide
Pentafunctional		
Diethylenetriamine Adduct	Diethylenetriamine	Propylene oxide
Hexafunctional		
Sorbitol Adducts	Sorbitol	Propylene oxide or ethylene oxide
Octafunctional		
Sucrose Adducts	Sucrose	Propylene oxide

* Other compounds, including trimethylolpropane, trimethylolethane, pentaerythritol, ethylenediamine, sorbitol and sucrose, can also be used as initiators for block copolymers based on propylene oxide and ethylene oxide.

** Primary monoamines include aniline, cyclohexylamine and others. The compositions made from these amines and oxides are principally surface-active agents.

During the late 1980s, the polyurethane industry was faced with a major change in manufacturing practice to reduce foam blowing using chlorofluorocarbons (CFCs). The once widely used CFC-11 (CCl_3F) and, to a lesser extent, CFC-12 (CCl_2F_2), have been replaced with other blowing agents such as hydrochlorofluorocarbons (HCFCs) or other nonfluorocarbon-based blowing agents that have lower ozone depletion potentials. For some time, scientific data have shown that these "hard" fluorocarbons (they do not decompose) are the cause of an increasing depletion of the ozone layer above the earth's atmosphere.

The industry is working with two HCFCs: Cl_2FCH_3, called HCFC-141b, and $CHCl_2CF_3$, called HCFC-123. These materials decompose, permitting the production of polyurethane foams with acceptable performance characteristics, but they are more expensive than the hard fluorocarbons they are designed to replace. Commercial quantities of some of the new HCFCs have been available since 1992.

The industry has responded with the development of new manufacturing methods, machinery and auxiliary blowing agents to replace conventional fluorocarbon blowing agents. Flexible foam is produced using a water-blown technology—where the foam is blown by carbon dioxide gas generated when

water in the formulation reacts with toluene diisocyanate. Methylene chloride, acetone or hydrocarbons are sometimes used to replace some of the fluorocarbon. Rigid foams now use formulations with HCFCs replacing CFC-11.

MANUFACTURING PROCESSES

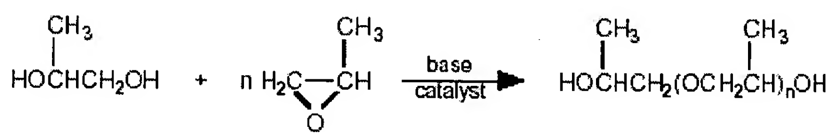
POLYOLS BASED ON PROPYLENE OXIDE

Polyether polyols based on propylene oxide (PO) are produced by the base-catalyzed reaction of propylene oxide with an initiator compound having active hydrogens (e.g., hydroxyl or amine groups). When small quantities of ethylene or other alkylene oxides are also present, block copolymers are produced.

Potassium hydroxide is the basic catalyst most often employed. The initiator used depends on the type of polyurethane (i.e., flexible, rigid or nonfoam) to be produced from the polyhydric alcohol. This reaction is carried out by a discontinuous batch process at elevated temperatures and pressures and under an inert atmosphere (i.e., under a nitrogen blanket). After the desired degree of polymerization has been achieved, the catalyst is neutralized and removed by filtration. The polyol is subsequently purified and additives such as antioxidants are added.

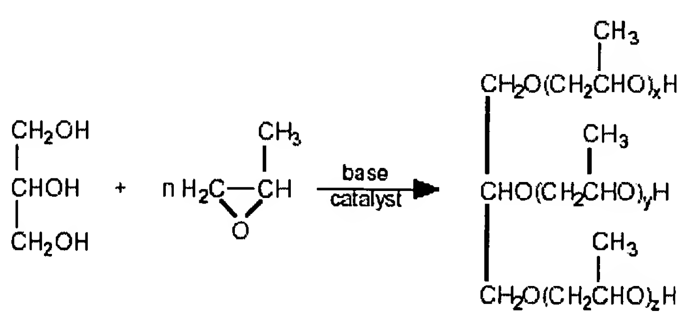
Simplified reaction equations for the major polyurethane polyether polyols are illustrated below.

POLYPROPYLENE GLYCOL (PPG)



	propylene glycol	propylene oxide	**polypropylene glycol (PPG)**
mol wt:	76.1	58.1	400-4,000

POLYOL ADDUCTS



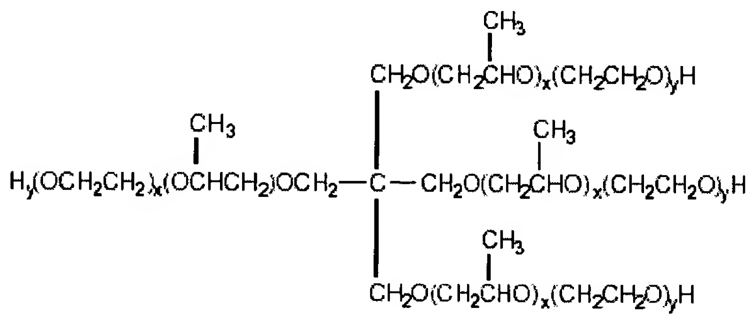
	glycerin	propylene oxide	glycerin adduct (n = x + y + z)
mol wt:	92.1	58.1	400-5,000

The manufacture of other polyol adducts (pentaerythritol, trimethylolpropane, trimethylolethane, sucrose and sorbitol) is similar to the above process. The manufacture of corresponding amine adducts generally follows the same process.

Block Copolymers

Block copolymers are commercially available that are initiated with glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, sucrose and several other compounds. They are based almost entirely on propylene oxide; however, the secondary hydroxyl groups are capped with ethylene oxide to yield terminal primary hydroxyl groups. Since primary hydroxyl groups are more reactive than secondary hydroxyl groups, these polyols are more reactive with isocyanates.

Block copolymers can be represented by the general formula shown below, where the initiator is a polyhydric alcohol (pentaerythritol initiator is shown below).



Small quantities of mixed and alternating block copolymers are also produced. In these block copolymers the ethylene oxide is incorporated into the alkylene oxide chains. These products may also be end-capped with ethylene oxide.

Tetrafunctional block copolymers initiated with ethylenediamine are also commercially available. The amine is reacted with propylene oxide to yield the totally hydroxypropylated ethylenediamine, which is further reacted with propylene oxide and then with ethylene oxide to form the desired polyether polyol.

Modified Polyols Based on Propylene Oxide

Polymer Polyols

Polymer polyols are also referred to as graft polymer polyols, graft polyols, or copolymer polyols; all of these terms are used to describe products that are basically stable dispersions of vinyl polymers in polyols. Polymer polyols are produced by the in-situ polymerization of a vinyl monomer in a base polyol.

The base polyol is typically a glycerin-initiated triol that has been end-capped with ethylene oxide (approximately 80-85% primary hydroxyl groups). Styrene and acrylonitrile are the vinyl monomers most often used. The styrene-acrylonitrile copolymers are chosen because in the preparation of graft polyols, acrylonitrile—due to its grafting tendency—provides a very important linkage between the vinyl polymer chain and the polyol chain. In addition to the graft copolymerates, the polymer polyol contains the homopolymers of styrene and acrylonitrile dispersed in unaltered polyether polyols. The styreneacrylonitrile solids content of the polyol ranges from 5% to 45%. The solids content of the polyol depends on the end-use market; those having a high solids content are used

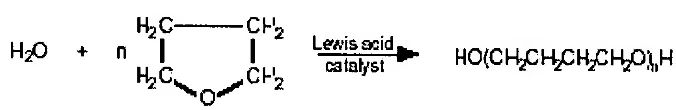
in carpet underlay while those having a lower solids content are used principally for molding applications such as automobile seating and furniture. Polymer polyols may be used alone but are typically used in blends with other highly reactive polyols in the production of high-resilience (HR) flexible foams. The principal benefits derived from the use of these materials are improved processing—due largely to a "cell opening" effect in HR applications—and enhancement of modulation, which in foams is measured as load bearing. Polymer polyols alone or in blends with conventional polyols permit the production of a range of foams with medium to high load-bearing properties. BASF, Dow, Lyondell Chemical and Olin are the primary producers of polymer polyols in the United States.

Polyurea Polyols

Another technically important group of modified polyols based on propylene oxide are the polyurea polyols, also known as PHD polyethers. Polyurea polyols are produced by the in-situ polyaddition reaction of isocyanates with amines in a base polyol. The isocyanate reacts more quickly with amines than polyols. Consequently, the isocyanate preferentially reacts with the amine (e.g., hydrazine) to form a urea group; the polyol functions only as a dispersion medium. The concentration of solids is limited by the viscosity of the product. However, polyurea solids content of 20-40% can usually be achieved. Polyurea polyols are used in blends with other highly reactive polyols in the production of HR foams and for reaction injection-molded (RIM) applications. Bayer is a producer of polyurea polyols in the United States.

POLYOLS BASED ON TETRAHYDROFURAN

Polytetramethylene ether glycol (PTMEG) of 650-2,000 molecular weight is prepared by the Lewis acid catalyzed polymerization of tetrahydrofuran.



	tetrahydrofuran	polytetramethylene ether glycol
mol wt:	72.1	600-3,000

PTMEG is, depending on its molecular weight, a liquid or a white waxy solid that melts to a clear liquid at 38°C (100°F). BASF Corporation, DuPont and QO Chemicals are the producers of PTMEG in the United States. The product is used in polyurethane elastomers and spandex fibers.

ENVIRONMENTAL ISSUES

Polyether polyols do not present an industrial hygiene problem, when used according to the relevant regulations. However, environmental issues are increasingly important in the polyurethane and polyurethane raw materials businesses. The industry has had to find replacements for HCFC blowing agents. It is now addressing the recyclability and reclaimability of used products. Some of the developing processes produce recovered polyols from polyurethane wastes.

HANDBOOK OF REINFORCED PLASTICS

of The Society of The Plastics Industry, Inc.

SAMUEL S. OLEESKY
Consultant for Reinforced Plastics
Los Angeles, California

and

J. GILBERT MOHR
Johns-Manville Fiber Glass Division
Waterville, Ohio

VNR
VAN NOSTRAND REINHOLD COMPANY
NEW YORK CINCINNATI TORONTO LONDON MELBOURNE

Chapter I-1

WHAT ARE REINFORCED PLASTICS?

A complete understanding of the field of Reinforced Plastics is almost impossible without a basic knowledge of the complete picture encompassed by the plastics industry as a whole. Broadly speaking, plastics are materials, generally of high molecular weight and of intricate molecular complexity, whose form and/or properties may be transformed into useful shapes or articles by the techniques of applying heat, pressure, or other manufacturing procedures. Still painting with a broad brush, we may divide plastics into two general categories, the thermoplastics and the thermosets.

Many analogies have been used to illustrate the differences between these two groups, none of which hold completely. For example, thermoplastics have been compared with candles, while thermosets have been compared with eggs. That is, a candle (thermoplastic) may be shaped, remelted, reshaped, and so on, until the molder has exhausted his possibilities. The egg, however, having once been cooked hard, cannot be "uncooked." This is the picture given to the layman, and it suffices as a general method of differentiating between the groups.

But for someone who wants to design or manufacture articles from these wonderful synthetics, so simple a division is not sufficient. Particular properties of each material must be known, so that intelligent use may be made of it and, most important to the plastics industry, misuse may be avoided.

Following is an alphabetical list of currently available plastic groups and a brief examination of each with respect to its properties and uses.

Acetal Resins

This resin, a thermoplastic, was introduced commercially in 1959. According to its producers, it is stiff, strong, has good fatigue properties, is resilient and tough, with low moisture sensitivity and high solvent resistance, offering excellent electrical properties. Molding temperature is 400 to 440°F, heat distortion temperature 338°F. When molded, it has a tensile strength of 10,000 psi, a compressive strength of 18,000 psi, and a flexural strength of 14,100 psi. At room temperature, it is highly resistant to common solvents. Acetal resins may be molded by injection or extrusion into many shapes, including rods, sheets, and tubes. Their uses encompass many fields, from pump impellers and lawn-mower wheels to instrument clusters and slide fasteners for clothing.

Acrylics

These widely used materials are probably best known by the trade names given by their major producers: "Plexiglas" (Rohm and Haas), "Lucite" (du Pont), and "Perspex" (Imperial Chemical Industries). They are, for the most part, methyl methacrylate polymers used as sheets, molding powders, ion exchange resins, and textile fibers. Depending upon the molding process, they are handled at temperatures between 300 and 500°F. They are classified as thermoplastic, and have tensile strengths of about 7000 psi, compressive strengths in the 12,000 to 18000 psi range, and flexural strengths ranging from 13000 to 17000 psi. Acrylics are used for glazing materials, for automotive parts, for name plates, knobs, dials, street lights, and a host of other applications.

Amino Resins

While this designation may be rather unfamiliar, the more widely used members of the amino family, urea-formaldehyde and melamine-formaldehyde resins, account for millions of pounds of annual uses in such diverse areas as appliance housings, dinnerware, buttons, electrical devices, plywood, and the paper industry.

They are thermosetting and have excellent resistance to heat and moisture. These properties account for many of their uses as surface finishes, as bases for baking enamels, and in table-top materials.

Alkyd Molding Compounds

These thermosetting compounds are based upon polyester resins, modified to provide easy handling and long storage life. As produced, they are available in three major forms: putty, fiber-reinforced, and granular. Compared with other thermosetting materials, their physical properties are not high, especially in tension. They do, however, have excellent electrical properties and dimensional stability so that, with proper design, many good applications are apparent. The greatest volume of alkyd molding compounds finds its way into the field of electrical components, such as switchgear, motor housings, circuit breakers, etc.

Cellulosics

A wide variety of cellulosic compounds is available in the thermoplastic molding field. These include ethyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate butyrate and cellulose nitrate. Probably the best known of the cellulosic films is cellophane, which is widely used as a packaging material and barrier sheet. They are subject to attack by various solvents, and some of them are readily soluble in cold water. Their wide diversity of chemical formulations makes them useful in such applications as automobile components, photographic films, and appetite-depressant tablets.

Epoxy Resins

Originating as commercially available materials about 1949, these thermosetting resins are rapidly assuming a major role in the fields of reinforced plastics, surfacing and adhesives. They have excellent resistance to attack by moisture and corrosive chemicals, and provide extraordinarily high strength to laminates and molded parts. The aerospace industry has used epoxies to great advantage in areas where other materials have provided unacceptable properties. For example, flexural and tensile moduli of two and three times those commonly developed with polyester laminates have been reported.

Ethylene Polymers

Currently being produced in the billion-pound-per-year area, polyethylene in its various grades is probably the most widely used of all thermoplastic materials, if not of all plastics. Available in three general grades, the low-, medium-, and high-density polymers, polyethylene is used in injection molding, film, sheeting, electrical insulation, pipe, coatings, fibers, tubes, blow-moldings and innumerable other applications. As an example of its diversity, it is found in sterilizable bottles for nursing babies and in slabs for shielding nuclear reactors. Its mechanical properties are relatively low, as is its resistance to heat.

Fluorocarbons

An unusual group of thermoplastic materials is included under the heading of fluorocarbons. They are relatively new in the plastics field, but have properties of great interest and potential. The major characteristics of interest include excellent thermal resistance and almost complete resistance to attack by solvents. Chemically, they are practically inert. They are available as molding powders and in aqueous dispersions. When molded, they have remarkable dielectric properties, exceptional resistance to adhesives, good toughness, excellent resistance to weathering, and zero absorption of moisture. Applications include laminating, coatings, extrusions, injection moldings, compression, and transfer moldings for insulation, electrical parts, sheet, film, printed circuits and temperature-resistant seals.

Furanes

Most of the resins with which the plastics industry works are derived from petroleum and its by-products. One group, however, originates in agricultural materials. These resins, the furanes (or furans) are the result of reacting furfuryl alcohol, a vegetable derivative, with various catalysts, aldehydes, ketones, dimethyl urea, and other reagents to produce resins, polymers, plasticizers, coatings, impregnants and adhesives. The thermosetting resins thus developed are liquid until polymerized. The furanes provide protective coatings for metals, mold coatings, and chemically resistant table-top materials.

Isocyanates

Strictly speaking, the isocyanates are not resins. They are, rather, a group of materials which, when reacted with any of a number of resins, produce the family of products known as urethanes. These compounds have tremendous value in the areas of coatings, elastomers, adhesives and foams. For example, flexible polyurethane foams have all but displaced cellular rubber as cushioning material for motor-vehicle and home upholstering in the furniture field. Rigid urethanes, frequently foamed in place, provide excellent insulation materials in refrigeration equipment. Urethane coating materials provide the abrasion resistance and gloss required, for example, in the production of patent leather. Elastomeric urethanes are used in gaskets, solid tires, encapsulants and similar applications. As metal-to-metal bonding materials, urethane adhesives develop excellent strength properties. They are also applied extensively in bonding fabrics, leather, ceramics and glasses.

Phenolics

Historically, the phenolic resins are among the first of the synthetics. They are the products of various reactions between phenols and aldehydes, and represent a high volume of the thermosetting materials in current use. They go into molding compounds, bonding materials, impregnants, castings, structural board, insulating and electrical products, and a host of other industrial applications. When molded, they have high strength, relatively good heat resistance, and excellent electrical performance.

Polyamides

These thermoplastic resins are better known as nylon, and the applications run the gamut from switchgear and household appliances in the industrial field through sporting goods, such as football helmets, to textile fibers for use in lingerie. There are at least half a dozen types of nylon, based upon as many chemical reactions, but the general family is derived from the reaction of various diamines with dibasic organic acids to form linear chains containing amides. The particular reagents used result, of course, in different properties, but generically nylon has excellent molding properties, offering abrasion resistance, toughness, impact strength, electrical insulation and good chemical resistance.

Polycarbonates

Still another new member of the thermoplastic family of resins is the polycarbonate group. Its primary suppliers claim that it has excellent dimensional stability under varying conditions of temperature and humidity, high (280 to 290°F) heat resistance, good electrical properties and high impact strength. Chemically, the polycarbonates consist of bisphenol radicals joined together by carbonate linkages to form large molecules. Their uses include electrical applications, business-machine housings and gears. Because of their transparency, they are also available for use in instrument windows and lenses. High creep resistance makes them good materials for fasteners, such as bolts and rivets.

Polyesters

This family of thermosetting resins is the basis for the entire Reinforced Plastics industry, and much more emphasis will be placed upon their properties and processing in later sections of this handbook. Essentially, a polyester is the result of the reaction of a dicarboxylic acid with a dihydric alcohol, but the variations of this reaction encompass many basic materials, resulting in resins with widely diversified properties. In general, however, the important characteristics of polyester resins include good electrical and physical properties, easy handling (polymerizing at room temperature, if desired), solidifying without evolution of gaseous or liquid by-products, and good dimensional stability. By addition of small amounts of other materials, polyesters may also be made flame resistant, heat resistant, corrosion resistant, and stable against the effects of light and weather.

Polyolefins

Chemically classed among the simplest of polymers, this group includes polyethylene and polypropylene, which account for a high percentage of the volume of the plastics materials and products marketed today. Polyethylene is available in three general classifications, low, medium, and high density, and is used in all three classes for sheet, film, tubes, pipe, coatings, filaments and commercial applications such as blow-molded squeeze bottles, packaging, tanks, battery separators, etc. A similar thermoplastic polymer, polypropylene, has somewhat better mechanical and thermal properties than

polyethylene. It is relatively new (1957), but shows promise of many applications, having already thoroughly invaded the field of piping, valves and chemical applications. Under the same conditions as polyethylene, the heat distortion temperature of polypropylene is about 50°F higher, showing a 230° distortion point, as compared with 180° for polyethylene of the high-density type.

Silicones

Here is a group of thermosetting resins which bridges the gap between the field of organics and that of inorganic materials, producing properties more useful than those of either group alone. Chemically speaking, the silicones are classed as organopolysiloxanes, consisting of alternating silicon and oxygen atoms, with organic groups attached to the silicon atoms. The nature of the organic groups will determine the properties of the particular silicone resin, making it a liquid, a solid, or an elastomeric material. Properties of these resins include high and low temperature stability, chemical inertness, water resistance, good electrical characteristics and resistance to deleterious environments. Silicones are used in laminations, as molding compounds, as release agents, in polishes, as lubricating fluids, as adhesives, as rubber substitutes for both high- and low-temperature application, and in a growing list of other fields whose variety is limited only by the imagination of the engineer.

Styrenes

Another family of high-volume thermoplastic resins are the styrene polymers. Styrene monomer is colorless, and this property is one of the factors in the large number of applications, since it lends itself to ready coloring, enabling the designer to produce almost any desired tint. Thus, polystyrene is used in toys, housewares, toilet articles, packaging, name plates, wall tile, refrigerator parts, etc. Normally, polystyrene has low strength, poor heat resistance, and crazes readily, but addition of other materials has overcome some of these disadvantages. The molecule is nonpolar, so that its dielectric properties are excellent, even when it is used in the microwave frequency range. Among its widest uses is that in the cellular form, where, as "Styrofoam," it is available for insulation, packaging, decoration and similar purposes. So-called "styrene alloys" are available in the form of acrylonitrile-butadiene-styrene (ABS) polymers, which have excellent mechanical and thermal properties. Styrene film is used for electrical insulation and for lamination purposes.

Vinyls

At least a billion pounds of these thermoplastic materials are produced annually in flexible and rigid form. They are available as vinyl chloride polymers and copolymers, polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals, polyvinylidene chloride, and a number of other molecular structures. Their uses are as diversified as their compositions, including electrical insulations, protective clothing, shower curtains, upholstering materials, protective and decorative coatings for metals, floor tile, toys, etc. Plastic pipe is extruded in both the flexible (garden hose) and rigid (plumbing) forms. Copolymer sheet is used in the field of vacuum forming, as well as for printing and embossing. In general, the vinyls have low resistance to heat, some of them distorting at points as low as 100°F.

Miscellaneous

In addition to the classes of resins listed, there are a number of materials produced whose volume represents only a small percentage of the over-all market picture. These include cold-molded organic plastics, low molecular weight hydrocarbons (coumarone-indene, petroleum, polyterpene), inorganic plastics (mica-based), ion exchange resins and protein plastics. Their properties, if required, may be found in any standard reference volume.

The information presented here is, of course, greatly simplified. It is not intended for engineering purposes, but only to give the designer an idea of the great variety of plastics available and some of their applications and basic properties. Our primary interest is in the field of Reinforced Plastics, and greatest emphasis will be placed upon that area.

What are Reinforced Plastics? They are a relatively new family of materials, but they represent a dramatic achievement in the story of mankind. For untold generations, man has used natural materials as the basis for his construction enterprises. He chopped down trees, quarried granite, made adobe bricks to build his homes, his communal houses, his office buildings, his monuments. He mined ores, refined the metals, and shaped them into his tools and his

structural shapes. But he was able to use only the physical properties available from the natural materials.

In Reinforced Plastics, man has, for the first time, created a new material of construction. He has reassembled molecules of natural origin into polymers whose properties he has designed. He has combined these polymers with natural or synthetic fibers of known properties into usable form whose composite structure provides him with strengths previously unattainable in natural forms of comparable weight. For example, a laminate composed of epoxy resin reinforced with glass fibers may be designed and fabricated with a strength-to-weight ratio ten times as great as that of a similarly shaped part made from steel.

COMPARATIVE PROPERTIES OF REINFORCED PLASTICS AND OTHER MATERIALS

Material	Specific Gravity	Tensile Strength × 10³ lb/in²	Young's Modulus × 10⁶ lb/in²	Specific Strength × 10³
Polyester-glass cloth	1.7	50	2.8	29.4
Steel	7.8	125	29.0	16.0
Duralumin	2.8	65	10.0	23.2
Douglas fir	0.5	10	1.4	20.0
Hickory	0.8	20	2.3	25.0

Essentially, then, reinforced plastics consist of combinations of resinous polymers (mostly thermosetting) with strengthening materials, such as glass in fibrous form, which provide the designer with a method of creating shapes or structures whose properties in any given direction, or in all directions, are both predictable and controllable.

As an example of the controllability of these properties, let us briefly examine a leaf spring, such as is used in the wheel suspension of a motor car. Its function is to absorb the energy of the car's vertical deflection and prevent shock of wheel impact from being transferred to the passengers. It requires great strength, but only in longitudinal flexure. The designer of a reinforced plastic spring may use fibers of glass, laid unidirectionally along the length of the spring, and bonded by an adequate resin, to create a product whose properties he can control by using the proper number of fibers in each area of the spring. There is no need to machine, forge, or heat-treat a strip of metal. He knows where the greatest strain will be placed upon the spring, and responds by inserting at that point the greatest number of strengthening fibers.

Similarly, if a spherical pressure vessel is required, the designer may wind his fibers into such a shape, bonding them in place in such a manner as to take advantage of the tensile strength of those fibers, without unnecessary waste of excess material in directions other than those required.

Reinforced Plastics have invaded almost every area of man's life, from sporting goods through transportation to building construction. They will continue to enter other areas, limited only by the will and the imagination of the engineer.

Combinations of exotic resins with reinforcements having good temperature resistance have resulted in the use of Reinforced Plastics for such applications as nozzles for rocket engines, heat shields for re-entry surfaces on space vehicles, nose cones, and laminates for structural and semistructural uses where metals or conventional laminates would lose their strength. In the field of recreational activities, directional properties of reinforced plastics are use to advantage in such applications as fishing rods, archery bows, shotgun barrels and diving boards. Ability of Reinforced Plastics to conform to compound curvatures is seen in their application to aircraft parts, automobile bodies, boats and furniture. Good insulation properties are demonstrated in their use in electrical and electronic housings and printed circuit boards, as well as in picnic iceboxes and refrigerator cars. Weather resistance is an accepted property of decorative panels for building construction and patio roofs, as well as for military housing and large rigid radome applications.

In modern advertising terminology, the word "miracle" is used to categorize the commonplace product or service, therefore it would be trite to describe Reinforced Plastics in those terms. But it would appear that the progress of mankind will be affected by the developments in the technology of Reinforced Plastics as much as—and possibly more than—developments in any other area of current industrial activity.

Although "Celluloid" (cellulose nitrate) was developed a century ago, the plastics industry as we know it today started during the first decade of this century when Dr. Leo Baekeland, in the United States, and Sir James Swinburne, in

England, first suggested industrial applications for the reaction products of phenol and formaldehyde, the so-called "PF resins." For many years these remained the cornerstone of the industry, and they are still of considerable importance today. During the last fifty years, and paticularly since 1930, enormous strides have been made and plastics now comprise many dozens of different materials, each with its own specific properties. It will be remembered that, shortly after the Second World War, plastics enjoyed a somewhat dubious reputation. This was largely due not to the materials themselves, but to an excess of enthusiasm which prompted manufacturers to use plastics simply for their own sake, without considering if the application was really suitable. There are no bad plastics, only bad applications.

Today, plastics in one form or another are used in almost every field of human activity. Metal, wood, glass, and other traditional materials have been replaced by plastics for many applications, not only because plastics components are often cheaper and easier to manufacture, but also because plastics are often the better material for the job. There are two basic groups of plastics: thermosoftening plastics, usually called "thermoplastics," and thermosetting plastics, or "thermosets."

Thermoplastics are softened by heating and set again on cooling without undergoing a chemical change; this physical change is reversible, i.e., by the application of further heat they revert to their original state. They can therefore be molded like wax or metal by heating in a mold and then cooling. Cellulosics, polystyrene, polyvinyl chloride, nylon and polyethylene are typical examples of thermoplastics. The techniques used for molding thermoplastics include injection molding, extrusion, hot calendering, casting, and drawing (vacuum forming). The heat resistance and tensile strength of thermoplastic materials are often low, and they are generally not suitable for most load-carrying structural purposes.

Thermosetting plastics, on the other hand, become increasingly infusible on heating. They undergo a chemical change which is not reversible. This reaction is called polymerization or curing, and is characterized by three stages: "A" stage, when the resin is still liquid; "B" stage, after heating, when the resin is a thermoplastic solid; and "C" stage, after further heating, when the resin is fully cured and has become an infusible solid. Thermosetting resins are generally molded under heat and very high pressures, and may be reinforced with paper or fabrics to form laminates. Although their heat resistance is often higher than that of thermoplastics, their impact strength is rather low, and by themselves they are not usually suitable for structural applications. Examples of thermosetting resins include phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde. All these materials cure through a condensation reaction during which a volatile by-product, often water or steam, is evolved. These by-products can cause blisters in the molding, and it is the prevention of such blisters which makes the use of high pressure necessary.

Unsaturated polyester resins—or polyester resins, as they are usually called—are thermosetting, but they have the great advantage that they cure through an additional polymerization reaction and do not evolve volatile by-products in the process. They can therefore be molded at low pressures, frequently only at pressure sufficient to keep the molding in contact with the mold, i.e., contact pressure. Their development made it possible to mold shapes of almost unlimited size at an economic price, which had previously been impossible.

When used alone, however, polyester resins are not strong or tough; but in combination with certain reinforcing materials, mainly some form of glass fiber, they exhibit properties which make them suitable as structural materials of considerable load-bearing capacity.

Although most thermosetting plastics are reinforced with fillers either in powder or fibrous form to give them improved mechanical properties, the term "reinforced plastics" is used almost exclusively to describe glass-fiber Reinforced Plastics, of which the overwhelming part consists of glass-fiber reinforced polyester resins.

Some of the reasons which make polyester resins and glass fiber such an excellent combination for reinforced plastics are:

a) Polyester resins are liquid and will therefore flow and impregnate glass fiber with little or no pressure.
b) Glass fiber is one of the strongest known materials and because it is glass, will not deteriorate even after long periods of time.
c) Glass fiber is easily crushed. This makes it unsuitable for high-pressure molding techniques. Since polyester resin can be cured with little or no pressure, glass fiber is therefore an ideal reinforcing material for it.
d) Fully cured polyester-glass-fiber moldings and laminates have excellent physical properties and better strength-weight ratio than many metals. Their good electrical properties and resistance to corrosion also make them suitable for many specialized applications. The manufacture of radomes for aircraft was, in fact, the first large-scale application of polyester-glass-fiber structures.

Various methods have been developed for the successful molding of glass-fiber reinforced polyester resins. They are fully discussed in later chapters, but mention is made here of the two most important techniques.

a) *Contact molding.* External pressure is not required. This method is ideal for small-to-moderate-size runs of large articles, such as vehicle bodies and boat hulls.
b) *Hot low-pressure molding.* More equipment is needed, but the molding cycle is shorter. It is used for the production of small to medium-size articles.

Polyester resins are cured by the addition of chemical compounds which control the polymerization reaction. These are:

a) Catalysts (sometimes called hardeners or initiators)—to initiate polymerization
b) Accelerators (sometimes called promoters) —used in conjunction with catalysts to enable polymerization to take place without the use of external heat.

Other ancillary materials which are frequently used are:

c) Mold release agents—to facilitate separation of the molding from the mold.
d) Powdered mineral or fibrous fillers—to provide special properties or to extend the resin.
e) Pigments or dyes to color the molding.

Excessive claims have frequently been made for Reinforced Plastics, as indeed, for many other materials. Every material has its own peculiar properties and its own specific applications. The fact that Reinforced Plastics can be successfully applied to a wide variety of end uses does not mean that they can be used indiscriminately to replace other materials. It would be foolish to pretend that Reinforced Plastics have no limitations. To help designers and fabricators to decide whether polyester-glass fiber is a suitable material for a particular application, the advantages and disadvantages may be summarized as follows:

Disadvantages:

a) All fabricating processes are slow by comparison with those used for pressed steel or sheet metal.
b) Cost of resin and glass is comparatively high. However, this is frequently offset by less costly equipment and by less highly skilled labor.
c) Mechanical and other properties of contact molded components tend to be inconsistent.
d) The rigidity of Reinforced Plastics is not very high, when compared with that of many metals.

Advantages:

a) Large complex shapes can be molded easily and cheaply.
b) Reinforced Plastics offer a greater freedom in design than most other materials.
c) Reinforced Plastics have a high strength-weight ratio.
d) Reinforced Plastics are extremely resilient. They do not dent like metal.
e) Reinforced Plastics have good weathering properties. They do not corrode, are resistant to many chemicals and to mold and fungus attack.

Reinforced Plastics should be seriously considered for production applications when the following conditions are involved:

(1) The expected production run will not exceed a limited number of parts. Depending on the size and complexity of the design, this number may be as small as a dozen or as great as 50,000. However, cost of tooling and possible subsequent operations should be assessed and compared with those for similar operations in Reinforced Plastics. When favorable cost and schedule ratios are apparent, Reinforced Plastics should be selected, provided that no compromise in quality and/or performance is implied thereby.

(2) A complete assembly in competitive materials may be replaced by a single molding in Reinforced Plastics. Frequently, it is possible to mold complex contours in one operation, when a metal part of identical or similar shape would require fabrication and assembly from several components. Reinforced Plastics demonstrate consistent advantages in this respect, in

that they afford considerable savings in finishing labor.

(3) Tooling for alternate materials would be unduly expensive or time-consuming. Because of the processes used in production of Reinforced Plastics, tool and mold requirements are usually much less stringent and expensive than those for metal. Consequently, cost may be as little as 10% of that used for metals. Concomitantly, tooling schedules are frequently measured in weeks, rather than months.

(4) Complex or intricate detail is required in the molded part. Purely by nature of the materials and processes involved, Reinforced Plastics will reproduce fine details of surface design and texture. The only reasonable limitation is that imposed by the effort expended in preparing the mold surface.

(5) Environmental conditions make performance and/or service life questionable. Where exposure to unusual temperatures, chemical attack, damp atmospheres, corrosion, or other degrading influences may be expected, investigation of Reinforced Plastics as a material for application should be seriously undertaken. Properly used, they provide long and satisfactory service life under conditions which would rapidly cause failure of conventional materials. Often, costs which might appear prohibitive as far as competitive materials are concerned are completely justified when examined in the light of projected service life, replacement expense, machine "down time" and similar factors.

(6) Weight and/or strength retention are problems. On a strength/weight basis, Reinforced Plastics will usually outperform most competitive materials. This is almost always an advantage in air-borne applications, and certainly is a favorable factor in most other forms of transportation, where prime movers must be selected on the basis of weight of cargo. In the area of strength retention, it is a fact that Reinforced Plastics maintain their ability to carry design loads at temperatures far below, or in excess of the temperatures at which metals, for example, will perform. They are not embrittled by exposure to cryogenic conditions, but actually improve their properties. And, at elevated temperatures where metals would become unserviceable, the plastic materials continue to perform adequately with little, if any, loss of strength.

(7) Impact damage is probable or possible. Reinforced Plastics do not deform when broken. When ultimate impact strength is exceeded and fracture occurs, repairs may be effected by simply mating the fracture edges and bonding or patching. No dents or bumps need be removed. A typical example here is an automobile fender or machine housing, which is subject to rough usage.

(8) Color is required. Again, by virtue of the processing techniques used, it is customary to include dyes or pigments in the molding. This provides uniform properties through the molded wall. No painting is necessary, damage from chipping or abrasion is eliminated, and good performance is insured. Finishing costs are, of course, often obviated, since final surface treatments, painting, and similar subsequent operations are unnecessary.

(9) Frequent variations or design changes are expected. As discussed earlier, tooling is often not complex, and minor changes can be made rapidly. When major changes are involved, replacement of tools is not nearly as costly as with competitive materials.

References

No.	Author(s)	Title or Periodical	Vol.	P.-Sect.	Year
1		"Polyester Handbook," Scott Bader & Co., Ltd.			1961
2		Molded Fiber Glass Body Company Presentation to Body Engineers' Society Meeting			1960

SECTION II

Resins, Catalysts, Promoters

Chapter II-1

POLYESTER RESINS

POLYESTER RESIN MANUFACTURE

Most of the raw materials used in producing Reinforced Plastic parts are themselves finished products. Resins are synthetically produced from materials which, in turn, do not occur in nature. Glass fibers and other reinforcements are derived from natural materials which have been reprocessed. Only the filling materials are comprised of naturally occurring substances. While this dependence upon "synthetics" may have the disadvantage of high raw-material cost, it has nevertheless made possible a unique and continually growing stream of products and processes based upon the encapsulation of a strong but friable filament with a weak but continuous liquid-that-becomes-solid matrix.

Resins in general are discussed in this section, and a separate chapter is devoted to each of the following types: polyester, phenolic, epoxy, silicone, acrylic, and miscellaneous, including melamine, furan, special thermoplastics, and inorganic types. In each resin chapter, the same general outline is followed, consisting of a description of general resin manufacturing procedure and control, resin properties, fields of usage and typical formulations, and, finally, resin chemistry and methods of catalyzing and promoting the cure.

Polyesters for use in Reinforced Plastics are available primarily in liquid form, although semisolid and solid resins are available for specific purposes. The liquid resins are available in room-temperature viscosities ranging from water-thin to asphaltlike; this is fortunate because the best properties of both resin and reinforcing agent are brought out by making the combination, the various viscosities being dictated by the end molding requirements. Also, the entire amount of monomer (reactive thinner) added to the resin becomes a part of the cured resin structure during polymerization (hardening or solidification due to chemical action).

Polyester resins result when certain organic acids or acid anhydrides, termed di- or polycarboxylic acids (two or more carboxyl (COOH) groups per molecule) are reacted with a specific class of organic alcohols termed polyols (two or more hydroxyl (OH) groups per molecule). Such a reaction is classed as an "esterification" process. An ester is the organic equivalent of the inorganic salt derived from the chemical reaction between an inorganic acid and base.

Equipment for large-scale production of polyesters consists of a ¼ in. to ⅜ in.-wall stainless-steel tank vertically aligned, approximately 8-ft. diameter and 10 to 12 ft. high (for 20,000-pound batch), with domed top and bottom, and 3 or 4 sealable entry ports or manholes in the top dome. A space allowance of 10 to 20% over batch size is made for head room in the top dome.

An 8 to 10 in. or larger diameter stirrer and 40-hp motor for agitation are mounted from the top dome so that the stirrer shaft extends vertically and is bearing-mounted at the bottom of the kettle; and stirrer blades are located at two or three levels along the shaft. A large steam- or hot water-jacketed condenser unit is also mounted from the top dome, with return piping and drainage to the atmosphere or a floor drain. The condenser must be occasionally steam-cleaned or blown out to prevent clogging.

Heating means are provided by a jacket around the outside kettle wall. The jacket is piped to a boiler and heat-exchange unit where heat is transferred to a high heat-capacity liquid (diphenyl and diphenyl oxide) which permits attainment of the required high reaction temperature without need for accompanying high pressure. Premixed gas and air combustion units and electricity are also used for heating in some kettle operations.

Cooling coils, facilities for exerting a negative pressure, and an inert gas (CO_2 or N_2) blanketing or bubbling system are also a necessary part of the reactor system. In some instances a separate cooling tank is included between the reactor and the thinning kettle. The latter is also made of stainless steel and has a stirrer shaft and motor and coils for cooling. It is located below and offset several feet from the main vertical axis of the reaction kettle. Piping arrangements from the bottom dome of the reaction kettle are made either for transferring material to the thinning kettle, or directly to cooling pans. Unloading by gravity or pump is carried out from the thinning kettle by piping from the bottom dome.

In a typical polyester producing plant, the reaction-kettle loading stations are on the third-floor level, the entrance to the thinning kettle on the second-floor level, and the thinning-kettle unloading stations at the ground-floor level. In a well-designed modern factory, adequate open space is allowed around the kettles at each level to facilitate movement of materials and personnel, and both the reaction and thinning units are independently suspended on separate scales with five-pound gradations for accuracy in batch control. Such a typical polyester producing plant is shown in Figure II-1.1.

In a brief follow-through of the processing of a polyester resin production batch, the stepwise progression noted is outlined below:

(1) Acids or anhydrides and glycols are successively charged, an inert gas is introduced by bubbling from the bottom and an inhibitor in solution is added. With mild heating, the acids rapidly melt in the glycol; some initial foaming occurs.

(2) A slow, stepwise heating cycle is followed over a 3- to 4-hour period, gradually raising the mix to the final reacting temperature. Acid number and viscosity control measurements are made during this period. Water is liberated and removed by the condenser.

(3) The mix is kept at 410°F (210°C) until the acid number is less than 50, or reaches the desired value (which may be lower), and also until the viscosity is within predetermined limiting values. Gel time is determined.

(4) If satisfactorily within specification, the mix is cooled to 210°F and transferred to the thinning kettle. Monomer is added to maintain usable viscosity and impart other desired properties required for handling and ultimate end

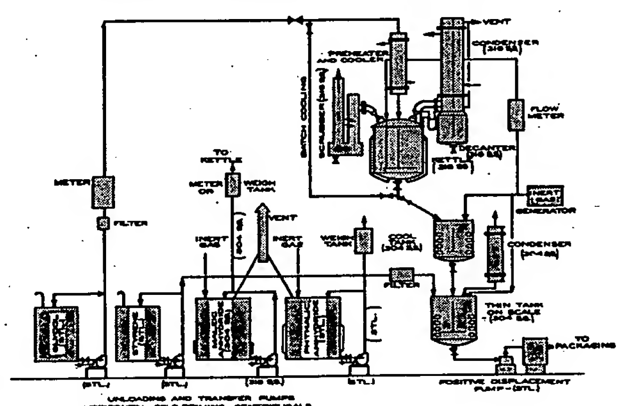


Figure II-1.1. Typical plant for polyester resin production. (*Courtesy Monsanto Chemical Company*)

use. Color, final gel time, and other pertinent properties are determined. The complete production cycle requires a minimum of approximately 8 hours.

It may be of interest to illustrate the over-all production efficiency of a polyester-producing unit. In producing what might be termed a representative or standard polyester resin batch, 1 mole or 1 equivalent of acid requires 1 mole or 1 equivalent of glycol for complete esterification. Hence, to produce a general-purpose, resilient-type resin, 1 mole of maleic acid anhydride (MW = 98) and 1 mole of phthalic acid anhydride (MW = 148) would react with 2 moles diethylene glycol (MW = 106, allow minimum of 5% extra) and 1 mole of water (MW = 18) would be produced for each mole of anhydride. Schematically:

$$\underset{98\text{ parts}}{\text{maleic anhydride}} + \underset{148\text{ parts}}{\text{phthalic anhydride}} + 2\,\underset{212\,+\,11\text{ parts}}{\text{diethylene glycol}} \qquad (1)$$

$$= \underset{433\text{ parts}}{\text{ester}} + \underset{36\text{ parts}}{\text{water}}$$

A portion of the excess glycol remains as part of the polyester, and the water is removed by the condenser, so that the batch yield is (theoretically):

$$\frac{433}{469} \times 100 = 92.3\% \qquad (2)$$

In producing the complete batch, including monomer, if 35% styrene monomer were added in the thinning kettle to produce resin with a working viscosity of approximately 20 poise, the batch and loss figures would be represented as:

	Input	Output	Loss
Reactor ingredients	469 parts	433 parts	36 parts
Kettle ingredients	above output plus styrene 152 parts	152 parts	
Totals	621 parts	585 parts	36 parts
Per cent yield, complete batch		94.1%	

If acids were used instead of the anhydrides, 2 moles of water would result for each molecule of acid, and the total yield after styrene addition would drop to 89.2%. This would be compensated for in part by the lower price of the acid compared with the anhydride, but some increase in reacting time would be required by removal of the additional water present in the acids.

In practice, a 1 or 2 per cent loss stemming from kettle, pumps, and handling equipment is realized. Also, blowing with inert gas removes some of the excess glycol. However, it may be noted from the above that the operation is an efficient one.

Polyester resins may also be manufactured using the same ingredients reacted in the presence of a suitable solvent such as xylene. The water is removed by azeotropic (mixed liquid) distillation, the xylene returning to the batch from the condenser. Reaction temperatures for this type of operation are lower, but the rate can be speeded up with certain acid catalysts. Some difficulty is experienced in complete removal of all the xylene from the finished polyester resin. Continuous-flow manufacture of polyester has been contemplated, but has been found impractical to date because of the excessive length of time required by the esterification reaction.

The many types of polyester with full range of divergent properties will be discussed more completely later in this chapter.

RESIN PROPERTIES

Of the total polyester output, liquid resins represent the largest sales volume, although some solid pulverized resins are produced. Certain specialized tests are performed on resins in the liquid state both during and following manufacture to make certain that the reaction has progressed satisfactorily, and to define other functions for control purposes. Other tests are performed on the solid polymerized cast resin (unreinforced) to indicate its probable behavior in the end use. Pulverized resins may be evaluated by the same group of tests where applicable.

Almost all tests involved have some value to the end user by helping him understand, evaluate, differentiate, or select resins to suit his own requirements. Performance properties of molded

parts are discussed in Section VIII. However, the particular group of tests described in this section applies only to unreinforced resins. ASTM or other pertinent test methods are referred to when necessary.

Tests on Liquid, Uncatalyzed Resins

Acid Number. The acid number is used to determine the progress of the esterification reaction. The excess glycol mentioned above is desirable in the batch to reduce the acid number before the reaction proceeds too far. During an esterification reaction, the acid number usually is first determined at a value of 80 and then further reduced to a value between 50 and 8 in the finished resin. Hence, it is also an indication of product uniformity for batch-to-batch control of a given resin.

The acid number is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize the free acids in 1 gram of the resin. In making the laboratory determination, a 50:50 alcohol-benzene reagent is made up, and 2 or 3 to 10 grams of resin (10 grams required for higher acid numbers) are accurately weighed into 50 ml of the reagent. A small amount of neutral acetone may be necessary to assist in dissolving some resins. The mixture is cooled and titrated with 0.2N KOH in methyl alcohol to a pH of 6.5 to 6.6 using bromthymol blue indicator.

Calculation: Acid No.

$$= \frac{\text{ml KOH} \times \text{N} \times 56.1}{\text{sample weight (in grams)}} \qquad (3)$$

Hydroxyl Number. Another function, the hydroxyl number, is related to the acid number, and is sometimes used to advantage in describing the properties or in checking the quality of a polyester resin. Hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1.0 gram of the resin. It points up the low molecular weight content of the resin, and will give an indication of whether or not excess glycol was added to the finished resin to superficially adjust its finished acid number prior to shipment. Procedure for determining hydroxyl number is lengthy, but may be found in standard analytical works.[1]

Viscosity. Although there is chemically an optimum monomer content or dilution for a given amount of resin solids, monomer additions up to 45 or 50 per cent in a finished resin are possible without major deleterious effects on properties, and sometimes with improvements. This makes possible the fortuitous circumstance that, as stated previously, resin viscosity may be tailored to suit specific needs, and small adjustments may be made by further monomer additions or temperature variations. It is difficult and impractical to remove a monomer such as styrene once it has been added to a resin. Adjustments in resin viscosity are also possible using a suitable solvent which must be driven off before polymerization.

Resin viscosity determines workability with respect to fluidity and surface tension, or ability to penetrate and wet fillers or reinforcement. Different resins of the same viscosity will not necessarily exhibit exactly identical flow or penetrating characteristics, however. Very few resin applications, if any, depend upon viscosity for physical manipulation, as in the case of molten glass. Hence, most resin applications are concerned with either the extremely fluid or the completely solid states.

The viscosity of a simple (Newtonian) liquid (shear rate proportional to shearing stress) in absolute (cgs) units is defined as the force in dynes required to move, at a velocity of 1 cm per second, a liquid surface of 1 sq cm past a parallel liquid surface 1 cm away, overcoming the resistance to shear of the material filling the space between. If the force is 1 dyne under the conditions defined, the liquid has a viscosity of 1 poise (dimensions: grams per centimeter per second).

Kinematic viscosity (in stokes, dimension: square centimeters per second) is determined by dividing the absolute viscosity by the density of the liquid at the same temperature, and takes into account the true nature or cohesive forces in the liquid (ASTM-D445). In the room temperature and density range for liquid polyesters, values for kinematic viscosity in stokes are approximately 10 per cent higher than those for viscosity in poise.

Introduction of a physical or chemical thickening agent into a resin may be desirable for specific requirements, and produces a state known as thixotropy, which is defined as the property of certain colloidal gels or systems containing them of coagulating (becoming stiff and jellylike) when at rest, but becoming fluid when agitated or otherwise subjected to stress. Introduction of a thixotropic filler (1 to 2%) into a

5 to 8 poise resin prevents rundown from a vertical surface during the time the resin remains in the uncured state.

The third aspect of fluid-state variations concerns rheopexy, which may be defined as quick solidification of certain thixotropic fluids caused by a slow, repeated circular motion.

Of the several viscosity determination test methods applicable to polyester resins, the two most commonly used are:

(1) The more accurate rotating spindle viscosimeter,* in which shear is induced by a cylinder or disc rotated at three separate speeds, with the liquid resin at the required temperature, and

(2) Rate of bubble rise†, by which the unknown (sample) in a 10.7 × 114 mm corked glass tube (approximate dimensions) is inverted, and the rate of bubble-rise matched with that for known lettered standards at the same (77°F) temperature (ASTM D154 and D 1-545). The method has an accuracy of ±5%.

Figure II-1.2 shows a series of bubble viscometer tubes, and Table II-1.1 presents a listing of the bubble viscometer letter designations compared with corresponding viscosity units in stokes.

In the higher-temperature range (to 400°F), viscosity measurements may be made on unthinned or monomer-free melted resins (rotating spindle method) to obtain a curve which will be of value in predetermining efficiency of hot-dip applications. Various resin compositions, of course, exhibit different softening points and viscosity curves in this upper-temperature region.

The viscosity-temperature variation for a characteristic polyester containing approximately 30% styrene monomer with a 78°F viscosity of 28 poise (Z_4) will be ±1.7 to 2.0 poise for each degree F rise or decrease (respectively) in temperature. Hence, it can be seen that close, careful temperature control is important in making viscosity determinations.

The change induced by styrene monomer addition with the resin held at room temperature amounts to approximately minus 1.0 poise for each 1% of styrene added, and vice versa.

In addition to governing resin usage, viscosity

* Brookfield Model RVF; Brookfield Engineering Laboratories; Stoughton, Mass.

† Gardner-Holt Bubble Tubes (Lettered A_4 to Z_6); Gardner-Holt Laboratories; Bethesda, Md.

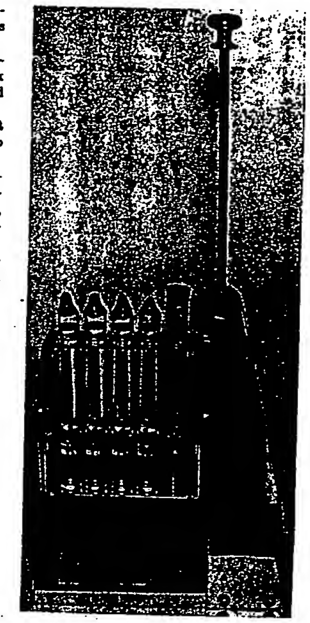


Figure II-1.2. Equipment for viscosity determination by bubble viscometer. (*Courtesy Gardner Laboratories, Inc.*)

measurement is also useful as a batch-to-batch control for both resin manufacturer and user. A plot of acid numbers and viscosity is usually made during the course of the esterification reaction. (See Figure II-1.3.)

Specific Gravity and Shrinkage. The specific gravity of a resin is the ratio of the weight of a unit volume to the same unit volume of distilled water (at 73.4 ± 2°F). For liquid resins, the specific gravity is most aptly determined using a 25 ml widemouth Hubbard-Carmick pycnometer for weighing water and resin at

TABLE II-1.1. COMPARISON OF BUBBLE VISCOMETER DESIGNATIONS WITH VISCOSITY IN STOKES AT 77°F

Bubble Tube Letter Designation	Approximate Kinematic Viscosity, Stokes
A_5	0.00505
A_4	0.0624
A_3	0.144
A_2	0.220
A_1	0.321
A	0.50
B	0.65
C	0.85
D	1.00
E	1.25
F	1.40
G	1.65
H	2.00
I	2.25
J	2.50
K	2.75
L	3.00
M	3.20
N	3.40
O	3.70
P	4.00
Q	4.35
R	4.70
S	5.00
T	5.50
U	6.2
V	8.8
W	10.7
X	12.9
Y	17.6
Z	22.7
Z_1	27.0
Z_2	36.2
Z_3	46.3
Z_4	63.4
Z_5	98.5
Z_6	148.0

73.4 ± 2°F to determine the ratio. The specific gravity value of a resin is used as a shipment-to-shipment or batch-to-batch control, and is also useful in determining the weight per gallon for packaging, shipping, or storage purposes.

Polyester resin specific gravities vary between 1.10 and 1.15 in the uncured state, and approach 1.25 in the cured (cast, not reinforced) state. This difference between the uncured and cured specific gravities makes possible a per cent shrinkage calculation:

$$100 \times \frac{\text{specific gravity cured—specific gravity uncured}}{\text{specific gravity cured}} \quad (4)$$

$$= \text{\% volume change.}$$

This figure is a valid expression of volume change only, because a polyester resin gels prior to any evidence of chemical polymerization reaction (such as exotherm). Another method developed at Purdue University for testing shrinkage of filled plastics from liquid (catalyzed) to hardened or cured state may be applicable.[5]

The volume change is not an accurate statement of the thermal expansion of a polyester casting nor of a laminate, however, and the value for this property should be determined with a dilatometer (ASTM E80 and C372).[28, 64]

The terminology, "polymerization" or "chemical" shrinkage describes the liquid-to-solid-state volume change (irreversible), while "thermal" shrinkage (or expansion) refers to that induced by temperature changes (reversible).

Water Content. Due to the fact that the original esterification reaction is reversible, a re-introduction of water under favorable conditions will convert a polyester into its original coreactants. At room temperature, polyester resins will actually dissolve several per cent of water by weight. Therefore, a maximum water-content specification of 0.1 or 0.15% by weight should be maintained for finished polyester resins for several reasons, chiefly (1) to make certain that the esterification has proceeded as required and that the condenser has not misfunctioned, and (2) that no mechanical failure of the piping system has occurred, permitting water to permeate the resin. Needless to say, water will cause delay and irregularity of the resin gel time (see pp. 21, 22, and 30), and also will weaken an end-use laminate, principally due to formation of steam during curing and exotherm.

Although other methods are available, the water content may best be determined in polyester resins by the Karl Fisher- Titration Method.*

Cleanliness. Cleanliness is necessary in resins intended for practically any use, and reflects

* Fisher Scientific Co., Pittsburgh, Pa.; and Wilkins-Anderson Co., Chicago, Ill.; Forte Engineering Company, Norwood, Mass.

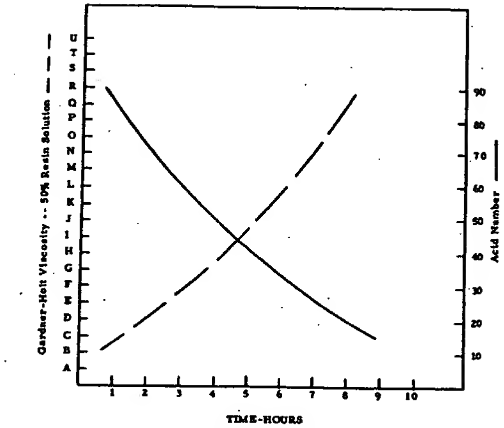


Figure II-1.3. Typical production-control curve; viscosity and acid number vs. reaction time.

the care employed in process control and also in selection of shipping containers. A cleanliness test is desirable to indicate the presence or absence of visible foreign material or gelled particles which would be considered as contaminants.

In evaluation for cleanliness, a 25 cc portion of resin taken with a Thief sampler is diluted with 225 cc of filtered acetone. The dissolved sample is then filtered through No. 4 Whatman paper on a 111 mm Buchner funnel, and the paper examined or compared with a preselected standard.

In another version, cleanliness may be evaluated by filling a clean, dry 29 mm I.D. × 125 mm test tube with resin, stoppering, and examining in or against a north light for the presence of gelled particles or foreign substances. An arbitrary standard for type or amount of permissible foreign material may be agreed upon by supplier and user.

Storage Stability. Periods of from only three weeks to as much as twelve months are guaranteed as storage stability for various types of polyester resins, six months being specified as the average uncatalyzed shelf life for general-purpose, styrene-modified polyester resins.

Evaluation is naturally made for the time required for the resin to increase in viscosity beyond the point of usability or to gel. Room-temperature storage stability is a function of composition, inhibitor, resin reactivity, and amount and type of accessory promoter added. The storage test should be conducted in the dark to exclude sunlight, which will induce polymerization.

Customarily, an accelerated test at 150°F may be correlated with and used to determine approximate room-temperature stability. Almost all commercial polyesters will gel in two or three to ninety-days' storage at 150°F.

Color. Many factors affect the color of liquid polyesters, such as type and purity of raw materials, temperature and length of time of the esterification reaction, cleanliness of equipment, etc. The color of polyester resins of differing compositions varies from water-clear to dark amber. For certain end-use requirements, fillers or promoters which alter resin color are some-

times added by either the manufacturer or the fabricator. Molding temperatures, catalyzing and exothermic changes also cause color shifts. However, it is desirable to maintain some control of color of the original resin for the purpose of uniformity. In the lighter or clearer resins intended for applications where decorative considerations or high light transmission are factors, color control of the base resin becomes even more important.

The Gardner-Hellige varnish comparative standards are generally employed as an in-process control for polyesters, the final resin color properties being judged by A.P.H.A. standards. Table II-1.2 presents a brief descriptive comparison of these two with other methods applicable in evaluating color of liquid polyester resins.

Index of Refraction. Refractive index (ASTM D542) is defined as the ratio of the speed of light in a vacuum to its speed in the substance considered. It has some relationship in polyesters to the possibility of matching the index of refraction of the impregnants or reinforcements. A perfectly transparent laminate has not yet been marketed commercially, however.

Difficulties arise from change of the refractive index when the resin is mixed with additional monomer, and from curing and shrinkage (density change), which in turn are affected by catalyst systems and temperature. Also, sizing materials on the glass are not completely removed, and the index for both resin and glass will differ for different wave lengths.

Index values for polyester resins fall in the range 1.5 to 1.55.

Dissolved Gas. The vacuum exerted on the thinned resin during the final stages of production (thinning kettle) removes dissolved gas down to amounts practical for almost all polyester application. Several uses, such as casting and architectural sheet, however, require nearly absolute freedom from dissolved gas,* and, hence, the following procedure is useful as an indication of the amount of gas contained in the as-received resin:

(1) Select a 75 cc resin sample and centrifuge to remove visible bubbles.

(2) Place in 180°F constant temperature bath for 3 to 5 minutes.

(3) Quickly examine for a thin train of bubbles rising up through the resin sample (similar to carbonated beverage bubbles). Nitrogen (N_2) gas is less soluble in polyesters than carbon dioxide; therefore, there is more likelihood of entrained gas in the resin if carbon dioxide has been used in production as the inert-gas blanket.

Table II-1.2. Comparison of Systems for Color Evaluation of Liquid Polyester Resins

System	Range for Polyesters	Reasons for Using with Polyesters	Remarks
Gardner-Hellige	1-18 Light to dark amber	For control during esterification process	Use viscosity sample in bubble tube. Evaluates by matching color value (ASTM-D1544).
APHA (Hazen)	0-500 (light to dark)	Finished resin control (without fillers or additives)	Use long-form Nessler tubes. Evaluates against platinum-cobalt solution standards for color intensity (ASTM-D1209).
Spectral transmission	0-100% at specific wave length	For special property measurements or comparisons	Use spectrophotometer. Excellent research tool, but measures to a high degree of sensitivity which is not in all cases practical for control and purchasing specifications (A.O.C.S. method Cc 13c-50).
Lovibond[illegible]	Red—50.0 Yellow—180.0 Blue—0.30	Provides separation of gray and green tints in polyesters by using the red and yellow tinted glasses. The gray and green tints are not resolved using the Gardner system.	Use color-reading apparatus described in A.O.C.S. official method Cc 136-45.

Tests on Liquid-catalyzed Resin

Gel-time Tests. Several tests, built principally around the "gel time" of a polyester resin, are employed to define its fundamental or primary behavior in the ultimate molding or forming operation, and, in addition, its storage stability, tank life, or gel-time drift.

Actually, the mechanism or physical changes by which polyester resins gel and cure is reduced to three separate phases, all related to and varying with the reactivity of the resin, the inhibitor, the catalyst used, and the curing temperature. Gelation is defined by the point at which the resin, after being catalyzed, ceases to be a viscous liquid and becomes a soft, elastic, rubbery solid. In layup or press molding, flow ceases after gelation, and no further changes may be made in any aspect of molding the product. Secondly, there is an intermediate stage in which the gel thickens or becomes slightly harder, and the temperature increases slightly, whatever the temperature range in which the molding is being carried out.

Thirdly, a strong exotherm occurs, brought on by the full result of the chemical action of polymerization. This accounts for the curing in some types of molding, and assists it in other types. Although polyester moldings and laminates are "set" and for the most part usable when reduced to room temperature following the exothermic reaction, ultimate properties are not always immediately developed, and in many cases a postcure is desirable.

Several different but related methods of defining gel time, or of using gel time to describe differences in various types of polyesters, or to compare similar types, have become known and are in general usage. Due to their similarity, an attempt has been made to tabulate these methods in Table II-1.3. A more detailed discussion of gelation and exotherm is included under "Catalysts" in this chapter.

While the gel-time methods presented in Table II-1.3 represent the optimum or usual requirements for the processes briefly referred to, it should be realized that variation in conditions and amounts of catalyst can greatly vary the resultant gel time. Hence, gel-time measurement is a manufacturing tool as well as a material control. Practical experience has shown the advantage of conducting gel-time tests at the temperatures employed in manufacturing or fabricating, as well as at 150° or 180°F, if the two temperatures are different.

Air Inhibition. The surface properties of a polyester resin immediately following gel and exotherm may be evaluated by first spreading a resin film on a glass plate using a film applicator (defines thickness of film to 0.010 in. or 0.020 in.), allowing it to cure at room or elevated temperature as required, and testing the surface for tack or stickiness with thin tissue paper or a probe. All polyesters are naturally inhibited by contact with the atmosphere during cure, due partially to styrene volatilization. Some compositions react less than others. For resins which must cure in contact with air (hand layup, spray-up), there is added, either in the thinning kettle or as-used, an ingredient that migrates to the surface during cure and forms a thin film which actually prevents contact of the resin material with air.

Tests on Cured Solid Resins

Mechanical Properties. The mechanical and electrical properties of laminated, reinforced polyester (and other) resins are of prime importance in actually describing end-use performance, and are fully discussed in Section VIII. However, the properties of cast polyesters (unfilled and unreinforced) are useful not only in comparing the type of resin (rigid, resilient, or flexible) but also in the control of properties. This is true because several properties of cast resins, although not as high in ultimate values as a fiber glass-reinforced laminate made from the resin in question, show greater deviation or fluctuation from specific values due to composition changes or cure variations. For this reason, cast resin properties can be used as a means of control, as well as fulfilling their specific function.

Table II-1.4 presents a comparison of mechanical properties of three representative polyester resins (rigid, resilient, and flexible) in the cast, unfilled, unreinforced state, with a typical cloth laminate made using the rigid resin. The 12-ply, 181-style, silane-treated cloth laminate will be considered a standard laminate for comparison purposes, and will be used elsewhere in this book.

The only test not referred to previously or not

TABLE II-1.3 METHODS FOR DETERMINING GEL TIME

	Catalyzed Stability	Room Temperature Gel Time	Intermediate Gel Time (150°F)	SPI Standard 180°F Gel Time	Cure Plate[C] Gel Time	Gel Time Drift
Definition	Time between catalyzing and gelation—in dark at 70°F	Time between catalyzing and gelation at 77°F (also 60 and 90)	Time between immersion in bath and gelation at 150°F	Time elapsed for resin sample to rise from 150°-190°F	Time between dropping sample and solidification at plate or mold temperature	Successive lengthening or shortening of gel time of specific resin sample (R.T. or SPI gel)
Purpose	To determine tank or pot life; used as a control	Determine usability at R.T. after catalyzing for hand layup and other R.T. curing resins	To determine time for formability and as control in resin, for architectural sheet	Provide standard method of measuring gel time and exotherm for all polyesters	To determine flow time of resin batch at molding temperature for matched-die and premix resins	To determine efficacy of promoters and stability of resin compositions over extended periods
Test bath or ambient (test) temperature	70°F	Controlled circulating water bath—60, 77, or 90°F ± 1°F	Controlled circulating water or oil bath, 150°F ± 0.5°F	Controlled circulating water or oil bath, 180° ± 0.5°F	Molding temperature—225-310°F ± 1°F as required	Use either room temperature or SPI-180° gel time test
Sample size and container	50 gm in 2-oz. glass bottle	100 gm in 150-ml beaker	100 gm in 150-ml beaker (extra 100 gm in paper cup for corresponding R.T. gel time if required)	100-gm sample, catalyzed and poured 3 in. deep into 19- x 150-mm glass test tube	Drop covering 0.5 sq. in. on plate or mold surface	R.T. or SPI-180° as required
Promoter/catalyst	BPO—1%	Cobalt naphthenate + accessory promoter and MEK[D] peroxide—1% or as required	Promoter—0.25% BPO[D]—0.25% CHP—0.50% (typical)	BPO—1%	BPO—0.7-1%	Same as R.T. or SPI-180°
Gel time range (Typical)	1-14 days	10 min-8 hrs per catalyst type resin and temperature	150°F—4 min to 20 min. R.T. potlife to 2 hr	3-6 min	10 to 30 sec (Add aluminum powder, or stroke to cure)	Express as % over or under initial gel time
Exotherm (Typical)	Not determined	Not usually determined	300°-450° (use temperature recorder plus mechanical gel time meter)[A]	300°-450°F (use recorder and standard SPI gel time test procedure)[B]	Not determined	Determine as required

Notes:

[A] Recorder—Leeds & Northrup Speedomax (Type G) with chart No. 206, or equivalent.
Mechanical-electrical gel time meters:
a. Sunshine meter, Sunshine Scientific Company, Philadelphia, Pa., (rotating rod).
b. Mol-Ras meter, American Petrochemical Corp., Minneapolis, Minn. rising and falling ball).
c. General Electric meter, General Electric Co., Schenectady, N. Y. (rotating rod).
d. Stainless-steel needle type thermocouple probes are available from Leeds-Northrup or Minneapolis-Honeywell.

[B] "The SPI Procedure for Running Exotherm Curves—Polyester Resins" was approved as a standard method for determining gel times and exotherm curves by the Reinforced Plastics Division on September 3, 1960. The method is duplicated at the end of this chapter[4] (Appendix II-1.1).

[C] Standard cure-plate: Thermo-Electric Co., Cleveland, Ohio.

[D] MEK—Methyl Ethyl Ketone Peroxide
BPO—Benzoyl Peroxide
CHP—Cumene Hydroperoxide

TABLE II-1.4. TYPICAL MECHANICAL PROPERTIES OF REPRESENTATIVE UNFILLED, UNREINFORCED POLYESTER CASTINGS COMPARED TO PROPERTIES OF A REPRESENTATIVE FIBER GLASS-REINFORCED LAMINATE†

	Cast, Unreinforced Genl. Purpose, Rigid	Cast, Unreinforced Resilient	Cast, Unreinforced Flexible	Laminated, Reinforced (181 Style, Silicone Trt. Cloth) GP Rigid Resin	ASTM Test No.
Flexural strength, psi	16,700	16,000	*	58,700	D790
Flexural modulus of elasticity, psi × 10^6	0.69	0.40	*	3.0	D790
Tensile strength	10,500	7,000	1,360	45,000	D638, D651
Tensile elongation at break, %	1.8	8	65	2	D638
Compressive strength, psi	22,500	30,700	*	35,400	D695
Impact strength Ft-lb/in. notch, Izod	0.4	0.5	1.5	25	D256
Water absorption, 24 hr, %	0.21	0.23	0.40	0.13	D570
Heat deflection temperature under load (264 psi), °F	194	140	*	392	D648
Specific gravity	1.22 (Liquid = 1.13)	1.22 (Liquid = 1.14)	1.11 (Liquid = 1.05)	1.49	D792
Thermal expansion, 10^{-5}/°F (Range 50-125°F)	3.5	*	*	0.8	D696
Hardness, Barcol**	48	31	-0-	69	—
Resin content	100	100	100	28	—
Thickness	⅛ in.	⅛ in.	⅛ in.	⅛ in.	—

* Too flexible to test.
** Barber-Colman Co., Rockford, Ill.
† Data Courtesy Allied Chemical Corp.

included in ASTM designations is an impressor type hardness gauge test. (See footnote, Table II-1.4.)

RESIN CHEMISTRY

Resin Ingredients

The resins commonly referred to as unsaturated polyesters are mixtures of the true ester (long-chain polymer which results from the kettle reaction) dissolved in a polymerizable monomer which provides cross-linking units to unite the chains three-dimensionally. The two components coreact or copolymerize upon introduction of a peroxide (or equivalent type) catalyst to form a rigid, infusible thermoset.

The terminology, "unsaturated," indicates that unbroken double bonds are carried over from the original (acid) ingredients into the finished resin to provide points of reactivity; the double bonds (unsaturation) are opened up by the free-radical catalyst and unite with similar reactive chemical groups or units of the monomer. The final curing reaction is classed as "addition" polymerization because no by-products result, as opposed to phenolics (condensation polymerization).

Other resin types similar to unsaturated polyesters are briefly described, with the main differences shown:

Alkyd Resins. These resins are composed of original reaction ingredients similar to those of the unsaturated polyesters, but are modified with fatty acid oil types (linseed, soya oils) instead of monomers. No catalyst is added, but curing is accomplished by air-drying or baking in which oxygen provides the cross-linking means; thus the reaction is still a type of addition polymerization. The principal application of alkyds is in coatings and paint.

Some resins termed alkyds, but falling into the "unsaturated polyester" class, are monomer-modified and have had catalyst added. These are usually available as high-pressure molding compounds, ready-mixed with filler and reinforcement.

Saturated Polyesters. These are fusible resins in which none of the original ingredients are unsaturated, no monomer or catalyst is required, and the resultant linear (uncross-linked or non-three-dimensional) polyester is formed directly from the original melt into the product (fibers or film) and becomes a finished resin as it reaches room temperature.

Foam Polyesters. These do not need unsaturation, but require excess hydroxyl groups for cross-linking with a diisocyanate monomer (usually toluene diisocyanate). They also require different catalysts (amines). A liquid that is easily volatilized by a slight increase above room temperature is usually added as a blowing agent. An equally effective but more costly method of inducing foaming is by inclusion of excess carboxyl groups, which function both by cross-linking and by evolving carbon dioxide during gelation. Water, turning to steam, has also been used as a blowing agent together with CO_2 from the diisocyanates. Polyether resins are preferred for flexible foams.

Unsaturated polyesters are of major interest as reinforceable plastics due to the wide variety of ultimate end properties which may be obtained by varying the many potentially usable raw materials. These raw materials fall into four classes:

(1) *Unsaturated polybasic acids* are so termed because of the doubly bonded pairs of carbon atoms included in the aliphatic molecular structure, which contains two or more carboxyl (COOH) radicals. These introduce high reactivity and rigidity into the cross-linked polyester by providing the unsaturated double bonds. Anhydrides contain one less molecule of water than the straight acids, e.g., maleic acid.

(2) *Saturated aromatic polybasic acids*, when included as a polyester resin ingredient, modify to some extent the rigidity introduced by the unsaturated polybasic acids. As with styrene, the unsaturation contained within the benzene ring structure does not enter into polymerizations. There is no unsaturation outside the ring, the carboxyl groups being held by a single bond. These materials behave like saturated acids, but do not provide complete flexibility because of their rigid ring structure which is unlike the loose aliphatic structure of the saturated acids, e.g., phthalic and isophthalic acids.

(3) *Saturated dibasic acids*, in which carboxyl groups again exist in an aliphatic structure, but in which no unsaturation exists, are used to modify the resin reactivity by introducing longer chain lengths between the cross-linking junctures, resulting generally in the more resilient or flexible, higher molecular weight resins, e.g., adipic acid.

(4) *Polyhydric alcohols* (polyols), so termed because two or more hydroxyl (OH) groups exist on each aliphatic glycol chain, react with either type of dibasic acid to form the ester groups. Many glycols are usable for polyester synthesis, and properties imparted are varied, ranging from rigidity to resiliency through water and heat sensitivity, e.g., ethylene glycol.

In formulating for the esterification reaction,[34] one equivalent of acid requires one equivalent of glycol for complete esterification. A small excess (5 to 20%) of glycol is often used to bring the acid number down to a low value before polymerization has proceeded too far. The amount of water formed corresponds to the number of equivalents involved in the esterification. For each acid equivalent, one mole (18 grams) of water is formed. In the case of the acid anhydrides, only one-half mole of water is formed per acid anhydride equivalent (or, one mole per molecule of anhydride).

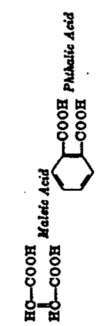
Hence, the organic reaction between acid and alcohol contrasts with the inorganic acid-base reaction in that the ester produced is vastly different from the corollary inorganic salt. The ester uniquely forms a polymer via a chemical growth process in which many single molecular units join to form a large, long-chain macromolecule, which is further added to and copolymerized by monomer and catalyst upon curing. The inorganic salt remains a single, low molecular-weight entity.

The fundamental dibasic acid (5) plus dihydric alcohol (6) to form the polyester chain (7) may be represented by the formulas on page 25.[36]

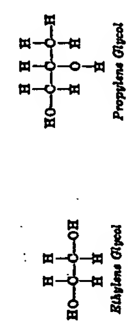
The understanding of polymer formation was greatly aided by development of the concept of functionality.[36] Functionality of polymerizing molecules is expressed as the number of reactive points in a molecule that can function in tying it to some other molecule. Basically, if the functionalities of either of two or more reacting molecules is only 1, no polymer will be formed. If the functionality of both constituents is 2, a thermoplastic will result; if one reacting molecule has a functionality of 3 or more and the other has a functionality of 2 or more, a cross-linked thermoset polymer can result.

The inclusion of molecular weight in any discussion of polyesters is apropos. Average molecular weight of the esterified polyester (before monomer addition and final cure) ranges in value from 800 to 5000.[37] Varying the relationship of the acids and alcohols provides the greatest control over molecular weight. A general increase in the molecular weight has a beneficial

(5)



(6)



(7)

Polyester chain: ester groups linking the carbon chains of alcohols and acids.
* Represents active sites for further reactions.

effect on the most important properties of the cured resin. However, permitting the molecular chains to grow too rapidly, or providing excessive chain branching (by use of polyhydric alcohols) provides a rapid build-up of molecular weight which is difficult to control,[20] and may result in undesirable pregelling during esterification.

Average polyester molecular weight may be increased by the following methods:[11]

a) Addition of inhibitors during esterification.

b) Reacting for longer time at lower temperatures.

c) Addition of the unsaturated acid to the reaction only after the saturated acid and glycol have been reacted to an acid number of 50 or less.

d) Blending a low (20) acid-number resin

with smaller proportion of unsaturation to a higher acid number (50), more reactive resin.

e) Refraining from use of a monocarboxylic acid or monohydroxy alcohol, which provide chain-termination or reaction-stopping groups.

Methods of determining molecular weight include viscosity measurements, light scattering, and sedimentation. Determining molecular weight or degree of polymerization is far from being an exact science,[27, 28] and there is only fair agreement between the different methods. Acid-number determination continues to provide the most practical indication of molecular weight, acid number values of 10 to 15 being indicative of higher molecular weight in resins.

Table II-1.5 presents a summary of information available in the literature regarding the effect on cured polyester castings (hence, laminates) when any particular acid or glycol is used.

TABLE II-1.5. POLYESTER RAW MATERIAL INGREDIENTS AND THEIR EFFECT ON CURED RESIN PROPERTIES

	Carbon Bonding	Functional Groups	EW	MW	Melting Point °C	Boiling Point °C	Formula	Esterification Reaction Time	Viscosity	Elastic Moduli	Heat Deflection Temperature	Exotherm
Maleic anhydride	U	4	49.03	98.06	52.8	199.6	$(CH)_2(CO)_2O$	M	H	H	H	H
Maleic acid	U	4	58.04	116.07	130.5	135*	$(CH)_2(COOH)_2$, cis	M	H	H	H	H
Fumaric acid	U	4	58.04	116.07	287	290	$(CH)_2(COOH)_2$, trans	M	H	H	H	H
Citraconic acid	U	4	65.05	130.10	91	—	$CH_3C(COOH)CHCOOH$, cis	S				
Itaconic acid	U	4	65.05	130.10	161d	d	$HOOCC(:CH_2)CH_2COOH$	S	M	H	H	H
Tetrachlorophthalic acid	S	2	151.95	303.90	254–255	363	$C_6Cl_4(COOH)_2$					
Chlorendic acid (HET)	S	2	194.43	388.86	208–210	—	$C_9H_4Cl_6(COOH)_2$			H	H	
Endomethylenetetrahydrophthalic anhydride	S	2	82.08	164.17	164–165	—	$C_9H_8(CO)_2O$			H	H	
Phthalic anhydride	S	2	74.06	148.11	131	285	$C_6H_4(CO)_2O$		M	M	M	M
Phthalic acid	S	2	83.07	166.13	208*	—	$C_6H_4(COOH)_2$	S	M	M	M	M
Isophthalic acid	S	2	83.06	166.13	330	Subl.	$C_6H_4(COOH)_2$	lo	H	M	H	H
Tetrahydrophthalic anhydride	S	2	76.07	152.14	99–100	**	$C_6H_8(CO)_2O$		M	M		
Hexahydrophthalic anhydride	S	2	77.08	154.16	35–36	158(17mm)	$C_6H_{10}(CO)_2O$		M	M		
Succinic anhydride	S	2	50.04	100.07	119–120	131(10mm)	$(CH_2)_2(CO)_2O$	S	L	L	L	L
Succinic acid	S	2	59.05	118.09	184	*	$(CH_2)_2(COOH)_2$		L	L	L	L
Adipic acid	S	2	73.07	146.14	153	**	$(CH_2)_4(COOH)_2$	S	L	L	L	L
Azelaic acid	S	2	94.06	188.12	106.5	**	$(CH_2)_7(COOH)_2$	S	L	L	L	L
Sebacic acid	S	2	101.12	202.24	133	**	$(CH_2)_8(COOH)_2$	S	L	L	L	L
Benzoic acid	S	2	122.12	122.12	122	249	C_6H_5COOH		L			
Glutaric acid	S	2	66.05	132.11	97.5	304	$COOH(CH_2)_3COOH$	S	L	L	M	L
Pimelic acid	S	2	80.08	160.17	103	272(Subl)	$COOH(CH_2)_5COOH$	S	L	L	L	L
Glycerol	S	3	30.70	92.09	—	290	$CH_2OHCHOHCH_2OH$		H	H	H	H
Ethylene glycol	S	2	31.04	62.07	−13.3	197.2	$HOCH_2CH_2OH$	S	H	H	H	H
Pentaerythritol	S	4	34.04	136.15	260	**	$C(CH_2OH)_4$		H	H	H	H
Propylene glycol	S	2	38.05	76.09	SC	188.2	$CH_3CHOHCH_2OH$	M	H	H	H	H
Butanediol-1, 4	S	2	45.06	90.12	19.6	228–231	$HO(CH_2)_4OH$					
Diethylene glycol	S	2	53.06	106.12	−8.3	244.5	$O(CH_2CH_2OH)_2$	S	M	M	L	M
Bisphenol A	S	2	114.14	228.27	153	—	$HOC_6H_4C(CH_3)_2C_6H_4OH$			M	H	M
Hydrogenated bisphenol A	S	2	120	236.33	130–156	—	$HOC_6H_{10}C(CH_3)_2C_6H_{10}OH$	S	H	M	H	M
Neopentyl glycol	S	2	52.07	104.15	120–130	—	$CH_2OHC(CH_3)_2CH_2OH$			M		M
Butylene glycol-2, 3; 1, 4; 1, 3	S	2	45.06	90.12	—	204	$CH_3CH(OH)CH_2CH_2OH$		H	M	M	M
Pentanediol (1, 5)	S	2	52.33	104.09	−15.6	242	$HOCH_2(CH_2)_3CH_2OH$		L	L	L	L
Triethylene glycol	S	2	75.09	150.17	−7.2	280–290	$(CH_2OCH_2CH_2OH)_2$		L	L		L
Dipropylene glycol	S	2	67.09	134.17	SC	229.2	$(CH_3CHOHCH_2)_2O$	M	L	L	L	H
Tripropylene glycol	S	2	96.13	192.3	SC	268	$CH_3CHOHCH_2OCH_2CHCH_3$		L	L		L
Isopropylidene bis (p-phenyleneoxypropanol-2)	S	2	172.22 / 129***	344.42	17	**	$(CH_3)_2C(C_6H_4$-$OCH_2CHOHCH_3)_2$					

	Gel and Cure Time	Hardness	Impact Strength	Flame Resistance	Light Stability	Curing Shrinkage	Flexural Strength	Tensile Strength	Compressive Strength	Per Cent Elongation	Surface	Water Absorption	Solvent Resistance	Alkali Resistance	Acid Resistance	Absence of Tack in Air	Adhesion to Glass	Styrene Compatibility	Catalyzed Stability	Color	Tendency to Crystallize	Crazing Resistance	Res. to Deformation under Load, Elev. T.	Flexural Strength at Elev. Temp.	Res. to Creep under Wet Condition	Specific Gravity	Cost	Cure Resin without Monomer	Electrical Properties
Maleic anhydride	S	ha	L	P		M	M			L		M		M					lo								M		
Maleic acid	S	ha	L	P		M	M			L		M		M					lo								M		
Fumaric acid	S	ha	L	P	G	M	M			L		M	H	M													H		
Citraconic acid												M															H		
Itaconic acid	S	ha	L	P		M				L		M		M					lo								H	Y	
Tetrachlorophthalic acid				I																									
Chlorendic acid (HET)				I	P								L	L	L					D		H					H		
Endomethylenetetrahydrophthalic anhydride				I																									
Phthalic anhydride	M	ha	M	P	P	M	H	H	H	M		L		G						B			L	L	L		L		
Phthalic acid	M	ha	M	P	P	M	H	H	H	M		L		G				H	M	B									
Isophthalic acid	M	ha	L	P	M	M	H		H	M		L		G			H		lo	B		H	I	I	A		M		
Tetrahydrophthalic anhydride					G	L			H	M		L																	
Hexahydrophthalic anhydride					G	L			H	M		L																	
Succinic anhydride	lo	so	M		M	H				H	so	H		G					lo	B									
Succinic acid	lo	so	M		M	H				H	so	H		G					lo	B							H		
Adipic acid	lo	M	M		M	H				H	so	H		G					lo	B							M		
Azelaic acid	M	so	H		G	H				H	so	H		M						M							H		
Sebacic acid	M	so	H		G	H				H	so	H		M					M	B							H		
Benzoic acid			H							H	so	H																	
Glutaric acid	M	M	M		G	H				H	so	H		G					S	B							H		
Pimelic acid	M	so	M		G	H				H	so	H		G					S	M									
Glycerol	S	ha	L				M	H	M																		L		
Ethylene glycol	S	ha	L				M	H	M												H						L		
Pentaerythritol	S	ha	L		G		M	H	M			L																	
Propylene glycol	S	ha	L		P		M	H	M			M		G				H	M								L		
Butanediol-1, 4																													
Diethylene glycol	M	so	M		M		H	H	H	M		H		G					S										
Bisphenol A						L	H	H	H	M			H	H	H	T	G												
Hydrogenated bisphenol A						L	H	H	L	M	T		H	H	H	T	G								G	L			
Neopentyl glycol						L	H	H	H	M			H	H	H	T	G												
Butylene glycol-2, 3; 1, 4; 1, 3	M	ha	L		P	H						M		G					lo										
Pentanediol (1, 5)	lo	ha	H		P	H				H	so	M		P					lo								H		
Triethylene glycol			H							H	so	M																	
Dipropylene glycol	M	M	H		P	H				H	so	M		P				H	lo										
Tripropylene glycol			H							H	so	H																	
Isopropylidene bis (p-phenyleneoxypropanol-2)																													G

U—Unsaturated
S—Saturated
SC—Supercooled
* Loses water to form the anhydride.
** Decomposes.
*** Practical equivalent as determined by esterification.
References: 4, 5, 6, 7, 8, 10, 11, 13, 14

Code: A—Approaches Epoxy Resins
D—Dark
G—Good
ha—Hard
H—High
I—Improved
B—Light
lo—Long
L—Low
M—Medium
P—Poor
S—Short
so—Soft
T—Tack Free
Y—Yes

Much of the data assumes starting with a resilient type resin (1:1 maleic:phthalic anhydride + 2.0 diethylene glycol) with modifications made toward rigidity with added unsaturated acids and toward flexibility by substituting the longer-chain saturated acids. Additional data[28] present specific performance values. Styrene monomer at 30% addition is further assumed, and all results represent tests on ⅛ in. thick castings cured with 1% BPO catalyst or equivalent.

Naturally, qualification of the entire resin composition is necessary for complete representation of the performance of any particular ingredient. Space limitations prevent inclusion of the many details available in the literature. Table II-1.5 attempts to represent the best performance known for a given ingredient, "high" or "good" signifying the top or best value of three grades, since this terminology is commonly used in the literature. Absence of any indicated performance of an ingredient for a specific property merely signifies that no reference was found in the literature cited.

Monomers

Table II-1.6 lists eight of the most commonly used or thoroughly investigated monomers, together with their physical properties and a qualitative summary of their influence on the physical properties of the cured polyesters in which they might be used as cross-linkers. As in Table II-1.5 (listing polyester raw material ingredients), many specific qualifications exist for monomers which are detailed in the literature.[5, 20]

In Table II-1.7 is presented for further reference a list of additional materials used or potentially usable as monomers to create a specific function or property. Styrene was originally used, and due to its economics it has become the most generally employed monomeric material. Actually, almost any of the common compatible vinyl-unsaturated organic compounds which will either homopolymerize or copolymerize with other reactive materials may be used as a monomer. In many circumstances, improvement of cured laminate properties is brought about by establishing the synergism of a mixed monomer system.

During the precatalyzed stage, the base resin-monomer combination is only a simple liquid mixture. After having been mixed in the thinning kettle, very little coreaction takes place, and as much as 99% styrene or other monomer actually present can be removed by exerting a vacuum.[20] During subsequent aging to six months, one or two additional per cent of monomer will combine with the base resin, detectable also as the amount removable by vacuum and by a rise in viscosity (molecular weight increase).

When the base resin-monomer mixture is catalysed and cure is under way, the unsaturated reactive groups of the monomer readily combine or copolymerize with the reactive groups of the base resin after the latter have been attacked and opened by the free radicals resulting from dissociation of the peroxide catalyst. The resultant three-dimensional, cross-linked thermoset structure may be made to yield many and varied properties depending upon the type and amount of both base-resin ester and monomer.

Between one and two moles of styrene are required for each mole of unsaturated acid in the original ester.[7, 20] A combination as low as 1:1 probably leaves some unreacted double bonds. However, the optimum styrene (or other monomer) content will vary with the per cent of unsaturated acid present and with the molecular weight of the base-resin chain. Practically, monomer additions of from 5 to 50 per cent by weight are generally made by the resin manufacturer with minor adjustments made by the end user. The ultimate monomer content is dictated by the end-use viscosity requirements, and the desired finished laminate properties are determined empirically.

Inhibitors

Some type of chemical inhibition is necessary in any one of four phases of polyester manufacture or usage:

a) Batch ingredients must be treated at the start of the esterification reaction to prevent random free radicals from inducing premature polymerization in the kettle.

b) Stability in storage is provided by adding the correct amount of the proper inhibitor. If the original inhibitor addition is depleted, more must be added in the thinning kettle, as determined by gel-time tests.

c) Extra inhibitor is sometimes desirable to nullify any tendency of the resin to gel prematurely due to heat generated in intermediate or end-use processes such as mixing, milling, or prolonged elevated temperature handling.

d) All monomers necessarily contain inhibi-

TABLE II-1.6. PRIMARY MONOMERS FOR POLYESTER RESINS

	Reactive Groups	Equivalent Weight	Molecular Weight	Boiling Point °C	Formula	Specific Gravity		Reactivity	Heat Deflection Temperature	Weathering Resistance	Light Stability	Elastic Moduli	Electrical Properties	Volatility	Compatibility with Ester
Styrene	2	104	104	145	$C_6H_5CH{:}CH_2$	0.902	30%	H	M	P	P	H	G	M	G
							50%		H	P	P	M	G		
Methyl methacrylate	2	100	100	100	$CH_2{:}C(CH_3)COOCH_3$	0.940		P		I	I			vh	
Vinyltoluene	2	118	118	172	$CH_3C_6H_4CH{:}CH_2$	0.897		H	H	P	P	H	G	L	
α-Methyl Styrene	2	118	118	163	$C_6H_5C(CH_3){:}CH_2$	0.906		M						L	
Dichlorostyrene	2	170	170	—	$Cl_2C_6H_3CH{:}CH_2$	—			H					H	
Divinyl Benzene	4	65	130	199.5	$CH_2{:}CHC_6H_4CH{:}CH_2$	0.929		vh				H			
Diallyl phthalate	4	123	246	290	$C_6H_4(COOCH_2CH{:}CH_2)_2$	1.13		H	H			L	G	L	
Triallyl cyanurate	6	83	249	162	$N{:}C(OCH_2CH{:}CH_2)N{:}C(OCH_2CH{:}CH_2)N{:}C(OCH_2CH{:}CH_2)$	1.113		H	vh				G		

		Wetting Characteristics	Cost	Flexural Strength	Tensile Strength	Resilience	Water Absorption	Flame Resistance	Mixed Monomers Required	Hardness	B-Staged	Chemical Resistance	Cure Rate	Color	Curing Shrinkage	Resistance to Crazing	Hot Strength
Styrene	30%	G	L	H		M	M		N	vg	N		F	Li	M		M
	50%			M		H	M								H		
Methyl methacrylate		G	H						Y		N		F	Li	H		
Vinyltoluene		vg	M	H	H	M	H		N	G	N			Li	M		H
α-Methyl Styrene											N						
Dichlorostyrene								G			N						
Divinyl Benzene									Y		N		I				
Diallyl phthalate			M						N		Y		S		L		H
Triallyl cyanurate			vh	H	H		vl		Y		N	G				G	

References: 4, 7, 8, 9, 10, 11, 12, 21

Code:

F—Fast L—Low P—Poor
G—Good Li—Light S—Slow
H—High M—Medium V—Very
I—Inconsistent N—No Y—Yes

TABLE II-1.7. ADDITIONAL MONOMERS

Monomer	Function or Remarks
1. Methyl acrylate	Improves light stability, weather resistance and laminate strength—comonomer with styrene
2. Ethyl acrylate	Similar to No. 1, laminates soft, so comonomer with styrene preferred
3. Allyl methacrylate	—
4. Acrylonitrile	—
5. Vinyl acetate	More reactive with maleate groups than styrene
6. Vinyl phenol	—
7. Diallyl fumarate	Reacts very poorly
8. Diallyl maleate	Reacts very poorly
9. *N*-Vinyl pyrrolidone	Improves flexural strength over styrene
10. Diallyl isophthalate	Faster curing than diallyl phthalate
11. Allyl diglycollate	High index of refraction; makes near-transparent laminates
12. Diallyl phenyl phosphonate	Similar to No. 11
13. Methallyl maleate	—
14. Diallyl carbate	Synergistic effect with triallyl cyanurate
15. Maleimide	High reactivity, good high-temperature resistance; tends to blister after long-term, high-temperature exposure
16. Triallyl aconitate	Contributes high-temperature resistance
17. Triallyl carballylate	Contributes high-temperature resistance
18. Triallyl phosphate	Contributes fire-resistant properties
19. Diallyl benzene phosphonate	Similar to No. 16
20. Triphenyl stibine	May contribute to fire resistance, maintaining transparency
21. Acetyl triallyl citrate	Provides long catalyzed pot life as monomer; also forms polymerizable resin with only maleic anhydride plus styrene and catalyst, yielding high-strength and modulus laminates at 30 psi, 320°F
22. Diallyl bicycloheptene dicarboxylate	Produces high-strength retention at 500°F; synergistic effect with triallyl cyanurate
23. Methyl methacrylate with phosphonate compounds	Similar to No. 11
24. Diallyl chlorendate	Contributes fire retardancy

References: 7, 9, 11, 13, 14, 23, 26, 57.

tors to prevent homopolymerization in storage. Some of the less reactive monomers do not require inhibition.

The actual mechanism of inhibition is not completely clear, but strong evidences and analytical procedures have made possible verification of theories and eventual categorizing of inhibitors into the following groups:

Stabilizing inhibitors are those which, due to rate of decomposition of or reaction with free radicals from catalysts, or reaction with active polymer growth centers, prevent polymerization only until they are used up, after which polymerization proceeds normally. The stronger types of stabilizing inhibitors are effective under both storage and polymerizing conditions, and their removal prior to catalyzing may be necessary in order to establish the desired cure rate. The second and preferred type are such that their effectiveness is terminated or stopped by heat, by promoters, or by other conditions which actually induce polymerization.

Retarders are a class of inhibitors which apparently slow polymerization inception or initiation, as do the stabilizers, but the retarders interfere permanently with subsequent chain growth, or completion of the normal polymerization cycle.

Table II-1.8 summarizes functions of both the stabilizing and retarding types of inhibitors as given in the literature, and also lists inhibitors used for monomers, which differ from those employed for the complete polyesters.

Inhibitors may be removed by washing, distillation, or filtration. The inhibitor originally included in the monomer is usually allowed to remain, and should not be of the type to seriously interfere with polyester polymerization.

Inhibitors are effective in concentrations of from 0.005 to 0.15% by weight. Solutions may be prepared using approximately 5% inhibitor solids in solvents, specifically, in a 50–50 mixture of styrene plus monomethyl ether of ethylene glycol, for ease in handling and batch addition.

The effectiveness of an inhibitor in a polyester resin may be determined by room- or elevated-temperature viscosity measurements at regular intervals over an extended period. Test methods used comprise the Brookfield viscosimeter, bubble tubes, and also observation of rate or stoppage of bubble rise in a 12-in. tube. Elevated-temperature gel-time tests (SPI standard method) are also employed.

Catalysts and Curing

Table II-1.9 illustrates the wide ranges of curing temperatures plus typical coordinated catalyst-promoter systems available for use with

TABLE II-1.8. INHIBITORS

A. Stabilizing Inhibitors	Function and/or Remarks
1. Oxygen	Large amounts compete with monomer for reactive polymer groups and inhibit, but may be overcome by adding a reducing agent or a material that surface-coats during cure. Small amounts of O_2 accelerate polymerization by formation of peroxides; O_2 also acts as comonomer probably by ultimately forming a polymer containing oxygen
2. Quinone	Probably the best and most effective inhibitor. Shows some instability in solution in presence of air, but does not exhibit any activation effect
3. Hydroquinone	Strong inhibitor in catalyzed polyesters; some activation effect with higher (0.05–0.1%) concentrations; requires higher temperature to end inhibition effect. Better than quinone for long-term uncatalyzed stability, but is probably actually slowly oxidized to quinone
4. T-butyl catechol	Strong inhibitor in catalyzed polyester; some activation effect with higher concentrations; probably actually oxidized to quinone
5. Ditertiary-butyl hydroquinone (2,5)	Effective inhibitor for esterification reaction, also for monomers, particularly acrylic
6. Copper and copper salts	General polymerization inhibitor; larger quantities of Cu (and other) metal powders promulgate violently rapid cure in presence of peroxide catalysts
7. Asbestos	Some natural forms act as polymerization inhibitors due to mineral impurities (brucite) but may be cleaned and purified to eliminate inhibitory effect
8. Chalk	General polymerization inhibitor
9. Ground glass	General polymerization inhibitor
10. Nitrites (organic and inorganic)	General polymerization inhibitor
11. Catechol	General polymerization inhibitor
12. Cellulose	General polymerization inhibitor
13. 1,4-Benzoquinone	General polymerization inhibitor
14. Naphthoquinone	General polymerization inhibitor
15. Phenanthroquinone	General polymerization inhibitor
16. Dinitrobenzene	General polymerization inhibitor
17. Trinitrotoluene	General polymerization inhibitor
18. Picric acid	General polymerization inhibitor
19. Phenyl β-naphthylamine	General polymerization inhibitor
20. Pyridine	General polymerization inhibitor
21. Phenyl hydrazine hydrochloride	Stabilizes well at room temperature and permits fast high-temperature cure
22. Trimethyl benzyl ammonium chloride	Prevents cracking and discoloration
23. *Para*-benzyl amino-phenol	General polymerization inhibitor
24. Di-beta-naphthyl paraphenyldiamine	General polymerization inhibitor
25. Trimethyl benzyl ammonium oxalate	Greatly prolongs catalyzed stability
26. Di (trimethyl benzyl ammonium) oxalate	Prolongs catalyzed stability
27. Trimethyl benzyl ammonium maleate	Prolongs catalyzed stability
28. Di (trimethyl benzyl ammonium) maleate	Prolongs catalyzed stability
29. Trimethyl benzyl ammonium tartrate	Prolongs catalyzed stability
30. Di (trimethyl benzyl ammonium) tartrate	Prolongs catalyzed stability
31. Trimethyl benzyl ammonium lactate	Prolongs catalyzed stability
32. Trimethyl benzyl ammonium glycolate	Prolongs catalyzed stability
33. Lauroyl pyridinium chloride	Normal inhibitor
34. Cetyl trimethyl ammonium chloride	Normal inhibitor

TABLE II-1.8—*Continued*

A. Stabilizing Inhibitors	Function and/or Remarks
35. Phenyl trimethyl ammonium chloride	Normal inhibitor
36. Trimethyl benzyl ammonium chloride	Normal inhibitor
37. Trimethyl benzyl ammonium hydroxide	Weak inhibitor
38. Alpha naphthol	Weak inhibitor
39. Di-beta-naphthyl paraphenylene diamine	Strong inhibitor
40. *Para*-xyloquinone	Reportedly permits inclusion of BPO catalyst in resin prior to shipment (limited stability, however)
41. *Para*-toluquinone	Same as 39
42. Quinone dioxime	Same as 39
43. Thymoquinone	Same as 39
44. 2,6-Dichloroquinone	Same as 39 (longest catalyzed stability of group)
45. 2,6-Dibromoquinone	Same as 39
46. Thymoquinone monoxime	Same as 39
47. Phenylene diamine	Used with alkyds
48. Mono-*t*-butylhydroquinone[43]	Good stabilizer for hot mixing resin with styrene, and is effective at lower concentrations without adversely prolonging resin cure, especially if hot-cure is used. Probably the best all-around inhibitor of this group (Nos. 48-54)*
49. 2,5-Di-*t*-butyl hydroquinone	Only slight effect on cured properties. Combines fair potency with a minimum effect on the curing of resins. Particularly useful in resins intended for fast room-temperature cures
50. 2,5-Di-*t*-amyl hydroquinone	Only slight effect on cured properties
51. *p*-Benzoquinone	Good stabilizer for hot-mixing resin plus styrene, but has objectionable effect on resin cure, as does hydroquinone; especially in room-temperature cures. Good inhibitor for storage of catalyzed resins. Also for uncatalyzed resins for storage at room and elevated temperatures
52. 2,5-Diphenyl-*p*-benzoquinone	Shows initial activation (i.e., viscosity increase) effect for first 10-15 days in polyester stored at 110°F—more so with uncatalyzed than catalyzed resin. This increase in viscosity may probably be expected and should be anticipated in establishing resin specifications. This material is an excellent stabilizer at high temperatures, as for hot-mixing resin with styrene, and also has minimum effect on subsequent resin cure. Is especially more satisfactory for use in room-temperature curing in concentrations 0.01 to 0.05%
53. 2,5-Diacetoxy-*p*-benzoquinone	—
54. 2,5-Dicaproxy-*p*-benzoquinone	—
55. 2,5-Diacyloxy-*p*-benzoquinone	Shows promise as a high-temperature stabilizer

* Note: Order of potency[44] for group (Nos. 48-54) compared to hydroquinone (No. 2) at 0.05% concentration, stored at 110°F:
Uncatalyzed Resin: 2 = 48 51 52 49 50 53 54
Catalyzed Resin: 51 2 48 52 53 54 49 = 50

polyester resins.[8] As indicated in the third, or "typical process" column, it may be readily noted that this adaptability accounts for the diverse channeling of these versatile resins into the many fields of usage in which applications have been found to date. It also presages a continuation of rapid annual growth of Reinforced Plastics by repeatedly offering a fertile field for inventiveness and well-engineered product development.

Although polyesterification takes place as a "condensation" polymerization reaction, the ul-

TABLE II-1.8—*Continued*

B. Retarding Inhibitors	Function and/or Remarks
1. Sulfur	—
2. Pyrogallol	—
3. Di or polyhydroxy phenols	—
4. Phenolic resins	—
5. α,β-naphthyl *para*-phenylene diamine	—
6. Tannic acid	Sometimes used in esterification to prolong reaction, permitting production of low acid number, high molecular weight resin
7. Ascorbic acid	—
8. Benzaldehyde	—
9. Alpha naphthol	—
10. Resorcinol	—
11. Certain color pigments and fillers	Pigment, filler, or resin cure system must be altered or substituted to eliminate the retardation effect

C. Inhibitors for Monomers	Function and/or Remarks
1. Sulfur	—
2. Hydroquinone	Best system: dilute styrene with inert low-boiling solvent, add hydroquinone, keep under nitrogen atmosphere. Remove inhibitor by distillation, filtration over carbon black, or reflux with an amine
3. Pyrogallol	—
4. Mono-, di- and tri-nitrobenzenes	—
5. Picramide	—
6. *Para*-aminophenol compounds	—
7. Triphenyl compounds	—
8. Phenolic sulfides	—
9. Hydroxylamine hydrochloride	—
10. Hexamine	—
11. Hematoxylin	—
12. Hematein	—
13. Phenylacetylene	—
14. α & β Coulderdrols	Equal to or better than Nos. 16 and 17 and also tertiary butyl catechol
15. Alkoxy derivatives of polyhydroxy aromatic compounds	—
16. Phenyl beta naphthylamine	—
17. Ditertiary-butyl *para*-cresol	—
18. p-hydroxydiphenylamine	Used with acrylic monomers
19. N-N'-diphenylphenylene diamine	Same as 18
20. Monomethyl ether of hydroquinone	Monomers containing MEHQ can be more readily polymerized or copolymerized without removal of inhibitor than those containing hydroquinone

References: 9, 11, 13, 19, 24, 44

timate thermoset cure of a polyester, as was previously shown, essentially takes place due to "addition" polymerization. This signifies that polyester and monomer units are successively and systematically linked due to a chain-joining, network-forming mechanism, referred to as vinyl (CH_2=CH) type polymerization, or that type originating from unsaturated double bonds.

The unsaturated double bond becomes the locus or point of development of an "active center"[20] from which polymer growth may propagate. Existence of the double bond does not signify that the molecular unit is stronger than any position where only a single bond exists, but only that double-bonded carbon atoms are more reactive. Only one valence bond is necessary to hold the carbon atoms together, and the other is at all times available for an addition reaction.[8]

Table II-1.9. Representative Temperature & Curing System Ranges For Polyester Resins

Type of Cure	Typical Catalyst: Promoter System	Designation of Typical Process
1. *Delayed or B-Stage;* Reinforcement saturated by resin with extended catalyzed stability (resin usually contains DAP monomer), cured at 235-300°F, 20-30 min.	1% benzoyl peroxide	Prepreg
2. *Room temperature-extended cure* (12-24 hr)	1% methyl ethyl ketone peroxide plus 0.05% cobalt naphthenate (or less)	Thick castings
3. *Room temperature-rapid cure* (20 min-2 hr)	0.4 to 1.5% MEK peroxide plus 0.1 to 0.5% cobalt naphthenate *or:* 1% BPO plus 0.05 to 0.1% dimethyl aniline	Hand lay-up or spray-up
4. *Intermediate cure (oven)* Stage 1: 150-180°F—20 min. Stage 2: 200-235°F—30 min.	0.25% BPO plus 0.8-1.0% cumene hydroperoxide plus 0.25% accessory promotor	Architectural sheet
5. *High-temperature cure (press)* Time—35 sec to 20 min Temps. 235 to 310°F Postcure at higher temperatures when required.	0.8 to 1.0% BPO or 1% *tert*-butyl hydroperoxide or 1% tert-butyl perbenzoate	Matched die and preform and premix; laminates

What means are available for generally triggering addition polymerization? There are four: thermal or photochemical means, for which no chemical catalyst is required; and either free-radical or ionic means, which involve catalysts.[a]

Free radicals are essentially responsible for polyester polymerization, and these are most generally supplied from decomposition by heating of, or action of a promoter on an organic peroxide. The peroxides are referred to as catalysts, but are not so in the truest sense, because they are consumed in the polymerization reaction. There is evidence that residual portions of free radicals exist in the network of the final product.

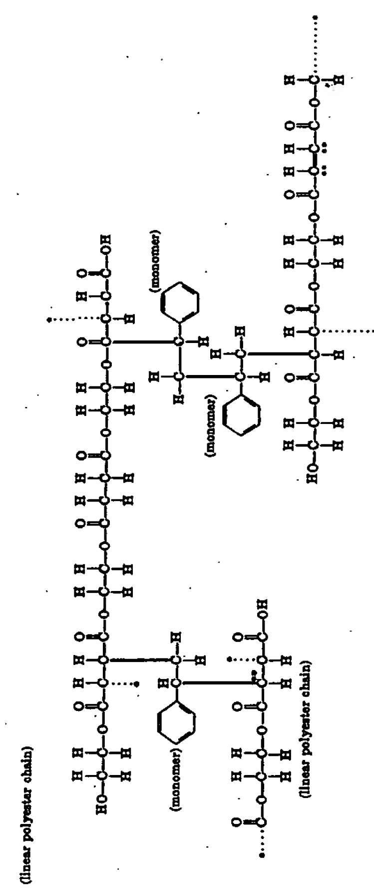
Assuming that a dibasic acid-dihydric alcohol-monomer polyester is activated with an organic peroxide, the following mechanism is set in motion:

a) The organic peroxide, represented as R—O—O—R′, where R and R′ may be an alkyl or acyl radical or hydrogen, decomposes by homolytic cleavage of the O—O bond to release the R—O and R′—O free radicals.[a]

b) The free radicals first react with the chemical inhibitor which has been previously added to the resin, since the inhibitor material must be chemically dissipated before any reaction between free radicals and the C═C double bonds can proceed. The number of free radicals available for polymerization can be directly influenced by accelerators (if present) and inhibitors, and the rate of peroxide decomposition (free radical production) must be such as to provide for the desired rate of consumption of the inhibitor, and the desired speed of polymerization.[a]

c) Apparently, the free radicals serve to open the double bonds in the polyester linear chain to set in motion that portion of the polymerization process designated as initiation. Either the opened double bonds react with the vinyl groups of the monomer, or the free radicals serve to also open (add to) these latter unsaturated C═C bonds, permitting them to perform their cross-linking function, uniting the polyester chains into a three-dimensional network. There is further evidence that free radicals may also, to some degree, react with the unsaturated monomer to form various products of decomposition.[a] The following formula represents the chain-joining and network growth schematically[a] (page 35):

d) The processes which are descriptive of



• Linear chain continues.
•• Active sites (unsaturation) for further reactions.

continuation of polymerization are termed "propagation" (or chain growth) and "termination." The functionality of the resin, as well as the types and concentrations of inhibitor, promoters, and catalyst determine the rate at which propagation proceeds. Also, the saturated dibasic acids, when included, function to limit chain growth by reducing the number of reaction sites available for cross-linking, thereby creating resilient or even flexible resins. Termination of polymer growth occurs via reactions designated as depletion, disproportionation, coupling and chain transfer." Also, high viscosity or viscosity increase during polymerization will cause termination.

Theoretically, the reaction of polyesters should go to completion with all double bonds reacted upon by free radicals, and complete cross-linking established under the most favorable conditions. However, in actual practice, as determined by iodometric analysis," the true amount of residual unsaturation (indicating how far the polymerization has *not* gone) has been traced in the actual curing of polyesters," and may be summarized as follows:

a) As stated previously, less than 1% of the unsaturated double bonds are reacted in the precatalyzed base polyester-monomer combination.

b) After catalyzing and polymer "initiation," when chain propagation has progressed so that 35 to 40% of the unsaturation has been taken up, gelation occurs. The gel hardens and initial volume shrinkage of the resin occurs as propagation proceeds, and 40 to 60% of the total unsaturation is converted.

c) An incomplete cure exists when a total of 80% of the unsaturation has been utilized without the development of full properties.

d) What may be considered as an optimum cure with full-properties potential realized occurs when 92 to 95% of the unsaturation has been converted. Neither extra catalyst nor post-curing will convert this slight amount of remaining unreacted material, which is sometimes removable from the cured resin by solvent extraction, but may be more accurately determined by analytical methods.

The failure of all unsaturated sites to become reacted during final cure accounts for the discoloration of polyesters upon weathering and long-term aging. The unreacted double bonds eventually take up oxygen due to the action of sunlight, etc., and peroxides are formed, creating a yellowish or amber color.

The physical and chemical changes occurring in polyesters during polymerization may be reduced to graphic representation by noting the rate of variation of resin temperature with time immediately after catalyzing and initiation of cure. The standard SPI 180°F exotherm curve (Figure II-1.4) has been adopted as a specific test to determine the several constants associated with the polymerization function. These parameters are defined as follows (see also Appendix II-1.1 and Table II-1.3):

a) *Gel Time:* Time elapsed as read on the actual exotherm curve between 150°F and 10°F above the (180°F) bath temperature (hence, 190°F). This definition applies for any desired reference (bath) temperature.

b) *Cure Time:* Time elapsed as read on the actual exotherm curve between 150°F and the time that the peak temperature was reached (also designated "total time" and "time-to-peak temperature").

c) *Peak Temperature:* The maximum temperature registered under the specified test conditions prior to the time that the exothermic heat is dissipated, and the exotherm curve starts a downward course.

d) *Kick-Off Temperature:* A reference point (±10°F) selected to compare the relative activity of polyester catalysts, inhibitors and promoters. It is defined as the inflection point on the exotherm curve at which a rapid rise to a peak exotherm occurs regardless of the bath temperature (kickoff temperature is not included as part of the standard SPI exotherm curve).

Acknowledging the foregoing study of resin chemistry, it is not difficult to visualize the value of the standard exotherm curve in comparing polyester resins with three varying degrees of reactivity. Table II-1.10 illustrates this.

Further, it is of interest to note that the standard exotherm curve is applicable to any reference point (using reproducible conditions) between room temperature and any elevated operating temperature. Frequently the exothermic behavior of a particular resin is determined both under 180°F standard conditions and at working temperature in order to acquire a more complete set of performance and control data. In addition, the exotherm curve is of substantial value in indicating the effect on a

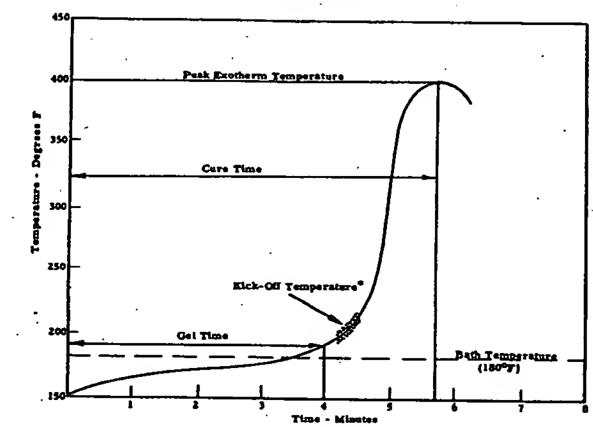


Figure II-1.4. 180°F standard SPI exotherm curve for polyester resins containing 1% bpo catalyst.

Note: Kick-off temperature is not included as part of the standard SPI gel-time test.

specific resin of changes in concentration of catalysts, promoters, and fillers. Table II-1.11 illustrates the changes induced by catalyst content and bath-temperature variations in the standard exotherm constants of a general-purpose resilient-type polyester (1.0 maleic anh., 1.0 phthalic anh., 2.2 propylene glycol, hydroquinone 0.013%, acid No. 45-50; 7 parts alkyd to 3 parts styrene, viscosity = 13 poise)."

Fillers (and reinforcements), being inert, lower the peak exotherm temperature of a resin formulation by absorbing heat from the reacting resin, but lengthen the gel time only if a room temperature cure is used, or if inhibitory effect is contributed.

Promoters are discussed later, since their function is to augment and expand the ranges of usefulness of the organic peroxide catalysts.

Many liquid and solid chemicals exist which are generally classed as organic peroxides. Since they are all by nature subject to rapid decomposition, handling precautions are necessary (see Section XI), and the most violently decomposable or shock-sensitive are combined with neutral but compatible materials (powders, plasticizers, solvents, or oils) to yield more stable solid, paste, or liquid commercially usable forms.

Price is probably the major factor governing selection of the appropriate organic peroxide for use in initiating polymerization in polyester resins. However, ease of handling and mixing, processing temperature and time, and rate of reactivity are also pertinent.

The many interesting properties found in the various peroxides are listed in Table II-1.12. Al-

TABLE II-1.10. VARIABILITY IN CURING CONSTANTS OF RIGID, RESILIENT AND FLEXIBLE POLYESTER RESINS (STANDARD 180°F SPI EXOTHERM CURVE TEST PROCEDURE, ONE PER CENT BPO CATALYST)

	Rigid Resin	Resilient Resin	Flexible Resin
Gel time, min-sec	4-28	5-30	5-12
Cure time, min-sec	6-26	7-30	8-40
Peak exotherm °F	422	358	307

Data: Courtesy Allied Chemical Corp.

TABLE II-1.11. EFFECT OF VARIATIONS IN CATALYST CONTENT AND BATH TEMPERATURE ON THE EXOTHERM CONSTANTS OF A GENERAL-PURPOSE RESILIENT POLYESTER

Variation in catalyst content, % BPO (Bath temp.—180 °F)	Gel Time, Min	Cure Time, Min	Peak Exotherm, °F	Kick-off Temperature, °F
0.5	10.3	12.4	390	205
1.0	5.6	7.6	393	192
2.0	3.6	5.5	408	180
4.0	2.8	4.2	415	155
6.0	2.2	3.2	400	138
Variation in bath temperature, °F (catalyst content = 1% BPO)				
180	4.4	6.3	410	200
212	1.6	2.7	430	200
240	1.3	2.1	430	200

though only approximately one-half the peroxides listed are in routine commercial use as polyester curing agents, all have been evaluated for potential or comparative performance in polyester resins on the basis of considerations given in the following discussion of the vertical column headings:

a) *Name, formula, availability data, and typical assays:* The available form, a price index, and concentration plus typical diluents are indicated.

b) *Half-life data:* In order to establish a meter of peroxide activity, the chemical kinetics were studied (Doehnert and Mageli) for decomposition of one-half the amount of a low (0.1 or 0.2 gm-moles of peroxide group per liter) concentration of each peroxide in benzene through a temperature range (120–320°F) corresponding to end-use polyester processing. The thermal decomposition of peroxides in solvents inert to free-radical attack has been shown to follow first-order kinetics. It is actually meaningless to refer to the time necessary for 100% of a material such as an organic peroxide to decompose, because theoretically, an infinite time is required. Therefore, half-life becomes a convenient parameter of peroxide activity.

Based on the residual peroxide concentration after specific test intervals at various temperatures, and applying first-order reaction rate calculations, the half-life ($t_{1/2}$) was in turn calculated from

$$t_{1/2} = \frac{0.693}{k} \qquad (9)$$

where k is the first-order rate constant. Following, the log $t_{1/2}$ was plotted against $1/T$ (T = absolute temperature) and showed essentially straight-line relationships for almost all the peroxides tested. Reference times of one minute, 10 hours, and 100 hours were then selected, after which the temperatures required for decomposition of one-half of the peroxide at those intervals were selected from the curves and tabulated. These half-life data are reproduced in Table II-1.12.

Each peroxide can thus be evaluated for the order of peroxide or free-radical activity in terms of a large number of other peroxides. Also, since the original data curves can be extrapolated, it is possible to estimate the half-life of a peroxide at temperatures where it was impractical to make experimental determinations. As an example, half lives for benzoyl peroxide were determined between 162 and 212°F, but the curve was further extended to provide data from which the following complete range of temperatures versus times for half-life decomposition was determined: 129°—100 hours; 162°—10 hours; 197°—1 hour; 230°—0.1 hour; 272°—1 min. From the data it is also noted that 2,4-dichlorobenzoyl peroxide (No. 3) is the most reactive peroxide, and would be expected to initiate reactions at the lowest temperature, while 2,5-dimethyl hexyl-2,5-dihydroperoxide (No. 14) would require the highest operating temperatures to perform effectively.

c) *Activation energies* (ΔE) were calculated in the same work for all those peroxides which showed first-order decomposition. The activation energy may be determined from measurements of the specific rate constant (k) at two or more temperatures according to the following equation or by plotting log k against the reciprocal of the absolute temperature ($1/T$), the slope of the resulting straight line being equal to $\Delta E/2.303R$:

$$\text{Log}\,\frac{k_2}{k_1} = \frac{\Delta E}{2.303R}\,\frac{T_2 - T_1}{T_2 T_1} \qquad (10)$$

where R = the universal gas constant (1.987 cal deg^{-1}-mole^{-1}).

Since for first-order decomposition (formula 9 for k applies), ΔE can be calculated from the slope of the line obtained by plotting log $t_{1/2}$ versus $1/T$. The degree of slope of these lines is a direct qualitative measure of the activation energy associated with each peroxide.

From a practical standpoint, peroxides with high activation energies will decompose over a narrower temperature range, or provide a larger number of free radicals in a given temperature range, than those with low activation energies. Hence, if an initiator is required that will show a narrow decomposition range, a high activation energy is desired. If a slow, gradual decomposition is required, a low activation energy would fill the need.

Although both relative peroxide activity and activation energy can be radically changed by the introduction of a specific accelerator, the information in the half-life and activation energy columns may be considered as basic data necessary for the choice of an effective initiator for any free-radical polymerization system.

d) *Kick-off Temperature:* In Table II-1.11, it was noted that the kick-off temperature was depressed with increased catalyst concentration, and that gel and cure times correspondingly shortened. Also, as specified, the kick-off temperature remained constant during changes in the bath temperature used as a reference point for the exotherm curve determination. The kick-off temperature data in Table II-1.12 are significant in that, by operating at or above the kick-off temperature range for a particular initiator system, rapid cures can be obtained.

e) *Gel Time Data:* Standard SPI gel time determinations for 1% of the commercial form of each peroxide tested were made in a 180°F bath (unless otherwise noted) using the reference polyester (formula on page 37). These data are included for purposes of coordinating gel times with half-life data and kick-off temperatures to further assay peroxide activity.

Determination of a reliable mathematical relationship between the rate of formation of active free radicals in a given peroxide and the gelation time of a normal unsaturated polyester would be difficult because of the many variables involved. However, a ten-hour half-life for many of the peroxides studied corresponded very roughly to the temperature at which a 15-minute gel time was obtained.

f) *Effect of Mixed Catalyst Systems:* Exotherm curves were run at 180, 112, 240°F. Total peroxide concentrations comprising an active oxygen content equivalent to that obtained with 1% benzoyl peroxide were investigated to determine subject data. Synergistic, intermediate-to-neutral, and inhibitory effects were noted. The synergistic or enhanced effect of the peroxide combinations and also those which showed inhibition are listed at the bottom of the tabulation, with reference made by number.

g) *Function and Remarks:* Those organic peroxides employed as catalysts in commercial polyester practice are so indicated, and the temperature range in which they have been found to be most useful is also classified. The functions of the organic peroxides whose major use is with polymerization systems other than those for polyesters are briefly referred to.

In addition to those peroxides cited in Table II-1.12, it has recently been brought to light that certain types of epoxy-silane finishes (applied to glass-fiber reinforcement) function as polyester polymerization initiators when used with or without peroxide catalysts. The epoxides themselves do not initially form peroxides, but undergo a free-radical reaction at the oxirane group.

Promoters

Figure II-1.5 has been prepared to provide an illustration of the effect of two members of a specific group of chemicals, termed "promoters," in activating decomposition of peroxide catalysts interdispersed with polyester resins at temperatures below the normal decomposition and activation temperature of the particular peroxide.

For methyl ethyl ketone peroxide, a half-life of 15 minutes at 293°C is exhibited, and gelation occurs in approximately 15 hours in a standard polyester resin at room temperature for a concentration of 1%. Curve *A* exemplifies how the room-temperature gel time may be shortened to 33 minutes by also incorporating 0.4% of the promoter, cobalt naphthenate (6% cobalt metal), and further shortened to 16 minutes by additionally intermixing 0.1 per cent dimethyl aniline (Curve *B*), termed the accessory promoter. Note the particular effect of the faster cure (by DMA) in raising the peak exotherm temperature.

It is fairly well-known that a simple one-promoter system such as cobalt naphthenate, used together with methyl ethyl ketone peroxide, will develop optimum properties at a slow rate after gelation and cure. In the early days of hand lay-up usage, eight hours' total mold time was required to produce a large item such

Table II-1.12. Properties of Organic Peroxides

	Available as Liquid (L) Solid (S) Paste (P)	Approx. Cost Per Lb Early 1960	Per Cent Peroxide (typical diluent)	Per Cent Active Oxygen	Decomposition Temperature °F in Benzene at Half-Life of: 1 min	10 hr	100 hr	Activation Energy (k-cal per mole)	Kick-off Temp. °F	180°F* SPI Gel Time (min) 1% Peroxide** Concentration	Function and/or Remarks
Diacyl Peroxides											
1. Benzoyl peroxide $(C_6H_5CO)_2O_2$	S (Gran) S (Powder) S (Powder) P	0.53 0.89 4.00 0.95	96 98 99 50 (TCP)	6.5 —	273	163	139	30.0	200	4.4	Widely used 0.1 to 2.0% in polyesters: R.T. (+ DMA, DEA or DMPT) and H.T. molding (225-275°F). Also used vinyl monomer and emulsion polymerization and miscellaneous applications
2. P-chlorobenzoyl peroxide $(ClC_6H_4CO)_2O_2$	S, P	5.00	50.0 (DBP)	2.4	272	167	136	30.6	220	10.7	May be used at temperatures slightly higher than those for BPO; also used to polymerize allyl-type monomers and vinyl chloride
3. 2,4-dichlorobenzoyl peroxide $(Cl_2C_6H_3CO)_2O_2$	P	3.00	51.1 (DBP)	2.3	234	129	99	28.1	170	5.3	For low-temperature, free-radical liberating catalyst with polyesters and vinyl-type monomers; also miscellaneous uses
4. Caprylyl peroxide $[CH_3(CH_2)_6CO]_2O_2$	L	4.45	90.1 (mineral oil)	5.5	233	143	117	31.0	160	2.9	Slightly faster gel and cure times than No. 5. Not widely used
5. Lauroyl peroxide $[CH_3(CH_2)_{10}CO]_2O_2$	S	1.40	98.0	3.9	240	144	115	30.7	180	3.3	Used in same temp. range as BPO, but preferred to BPO because: more soluble in monomers; activated at lower temp; absence of aromatic radicals; greater ease and safety in handling; improves some end properties such as light stability
6. Acetyl peroxide $(CH_3CO)_2O_2$	L	1.75	25.0 (DMP)	3.4	250	158	127	—	195	5.5	Interchangeable with Nos. 1 and 5, but used mostly with acrylics
Ketone Peroxides											
7. Methyl ethyl ketone peroxides $(CH_3COO_{1.5}HC_2H_5)_2$ and $(CH_3COO_2HC_2H_5)_2$	L	1.55	60.0 (DMP)	11.0	360	221	181	28.5	210	4.1	Widely used for R.T. cure with cobalt naphthenate and accessory promoters
8. Cyclohexanone peroxide $[C_6H_{10}(OOH)OO(HO)C_6H_{10}]$	S	3.00	85.0 (DBP)	11.0	not 1st order decomp.	198	160	—	230	5.3	More rapid R.T. gel than for MEK Peroxide with cobalt or metallic promoters; longer pot life
9. Bis (1-hydroxy cyclohexyl) peroxide $[CH_2(CH_2)_4C(OH)]_2O_2$	S	3.00	95.0	—	244 (1 hr in cyclohexanone)	—	—	—	220	6.2	Good peroxide for R.T. gel—fast gel and cure; high cobalt naphthenate sensitivity and lower peak exotherm; used approximately 1%
Aldehyde Peroxides											
10. Hydroxy heptyl peroxide $[CH_3(CH_2)_5CH(OH)]_2O_2$	S P	4.50	98.0 50.0 (DBP)	6.0	Not first order decomposition			—	250	7.0 (212°F)	Exhibits very fast gel and cure at room temperature + cobalt naphthenate, but not in general use with polyesters; nontoxic
Hydro Peroxides											
11. t-Butyl hydroperoxide $(CH_3)_3COOH$	L	2.05	73.1	13.7	334 (not first order decomposition)	250	220	—	270	8.5 (212°F)	Soluble in monomer, very stable peroxide and used for very high-temperature polymerizations (>310°F); volatile. Also used in emulsion-polymer processes.
12. p-Menthane hydroperoxide $CH_3C_6H_9C(CH_3)_2O_2H$	L	0.84	54.7	5.1	431	273	228	33.4	280	4.9 (212°F)	Slightly lower-temperature reactivity than CHP (No. 13); not widely used with polyesters, but mostly in rubber industry. Used with No. 20.
13. Cumene hydroperoxide $C_6H_5C(CH_3)_2O_2H$	L	0.80	72.7	7.7	421	318	270	30.0	250	4.7 (212°F)	Cures with moderate exotherm in 150-300°F range; higher exotherm above 320°F, so fast cures obtained; R.T. cure with 0.75% CHP, 0.3% manganese naphthenate and 0.08% dibutyl thiourea; shorter pot life; stable.
14. 2,5-Dimethylhexyl-2,5-dihydroperoxide $(CH_3)_2C(O_2H)(CH_2)_2C(O_2H)(CH_3)_2$	S	5.00	75 (H₂O)	13.5	498 (not first order decomposition)	310	259	—	290	5.5 (212°F)	Less active than No. 15 and approximately equal to No. 19 as polymerization initiator for high-temperature systems; nonvolatile.
Alkyl Peresters											
15. t-Butyl perbenzoate $C_6H_5CO(O_2)C(CH_3)_3$	L	3.05	98	8.1	331	221	189	34.7	245	9.8 (212°F)	Widely used in polyester premix, higher temperature stability (250-300°) than BPO, and will permit higher temperature in mixing without premature gelation; stable, neutral, nonvolatile.
16. t-Butyl peracetate $CH_3COO_2C(CH_3)_3$	L	4.00	75.0 (Benzene)	9.1	318	216	183	33.9	245	9.3 (212°F)	Moderately reactive; used at higher temperatures; major use: in polyethylene manufacture and end use: volatile.
17. t-Butyl peroxyisobutyrate $(CH_3)_2CHCOO_2C(CH_3)_3$	L	9.00	75.0 (Benzene)	7.5	263	174	144	33.3	210	6.3	Properties similar to BPO; used essentially with polyolefins.
18. Di-t-butyl diperphthalate $C_6H_4(COO_2C(CH_3)_3)_2$	L	4.50	80.0 (DBP)	5.2	318	221	190	27.7	250	13.3 (212°F)	For high-temperature systems—300°F and above; not widely used in polyesters; stable.
Alkyl Peroxides											
19. Di-t-butyl peroxide $(CH_3)_3COOC(CH_3)_3$	L	1.72	98.5	10.8	380	259	233	38.1	280	10.3 (340°F)	High-temperature catalyst; can be directly blended-in up to 194°F, allows controlled reaction rate; good source free radicals; soluble in monomers, but highly volatile.
20. Dicumyl peroxide $[C_6H_5C(CH_3)_2]_2O_2$	S (low melting) S (powder)	1.10-1.50 0.55	90-95 40 ($CaCO_3$)	—	340	243	214	40.6	280	20.9 (212°F)	Activates at lower temperature than No. 19 and slightly higher temperature than No. 15. Has long pot life, but slower cure; less volatile and very stable; used in premix, prepreg, and matched-die molding; some residual odor.

TABLE II-1.12—*Continued*

	Available as Liquid (L) Solid (S) Paste (P)	Approx. Cost Per Lb Early 1960	Per Cent Peroxide (typical diluent)	Per Cent Active Oxygen	Decomposition Temperature °F in Benzene at Half-Life of: 1 min	10 hr	100 hr	Activation Energy (k-cal per mole)	Kick-off Temp. °F	180° F SPI Gel Time (min) 1% Peroxide** Concentration	Function and/or Remarks
21. 2,5-Dimethyl-2,5-di(t-butyl peroxy) hexane $[(CH_3)_3COOC(CH_3)_2CH_2]_2$	L	4.00	95	10.5	246	246	217	—	240	25.2	Difunctional peroxide: activates at higher temperature than No. 15 and lower temperature than No. 19; useful in premix; promoted with tertiary amines (DMA) but inhibited by metal-promoters (Co); heat- and impact-stable. Permits hot mixing of premix at 140°F.
22. 2,5-Dimethylhexyl-2,5-di (peroxybenzoate) $[(CH_3)_2CO_2OCC_6H_4CH_2]_2$	S	4.80	93	7.7	234	212	180	—	200	7.8 (212°)	Difunctional peroxide, medium thermal activity, hence gives more complete cure than BPO (No. 1); useful for premix and prepreg; stable and nonvolatile.
23. 2,5-Dimethyl-2,5-di(t-butyl-peroxy) hexyne-3 $[(CH_3)_3COOC(CH_3)_2C]_2$	S	3.88	80.0 (inert filler)	6.4	279	263	228	—	280	11.2 (340°F)	Difunctional peroxide; activates at higher temperature than No. 21; used in hot mixing of premix (140°F) with added cobalt naphthenate; no posture odor. Also used in cross-linking polyethylene.
Dibasic Acid Peroxides 24. Succinic acid peroxide $(HOOCCH_2CH_2CO)_2O_2$	S	1.00	94.5	6.5	203 (in acetone)	151	111	33.8	—	13.0	Fairly stable, water soluble, used mostly in manufacturing of organic fluorides.
Miscellaneous 25. Isopropyl percarbonate $[(CH_3)_2CHOCO]_2O_2$	S	—	—	7.8	202	117	92	—	—	—	Activates approximately 45° lower than No. 1 (BPO); soluble in monomers, and solid material must be maintained in frozen state due to low stability; high reactivity permits less to be used; gives good color and stabilizes against weathering.

Effect of Mixed Catalysts in G.P. Resilient Polyester:
Synergistic Activity—180°F: 1-4, 1-4, 1-17, 7-10, 7-8, 1-7, 7-17, 1-7-17, 1-4-7;
212°F: 11-18, 11-16, 11-12, 11-15, 13-18;
240°F: 20-21
Inhibitory Effect—180°F: 6-14, 1-14, 5-14, 21-14, 8-14, 7-14, 7-11, 1-8, 9-8, 9-11, 9-10
* Unless noted otherwise.
** In commercial form.

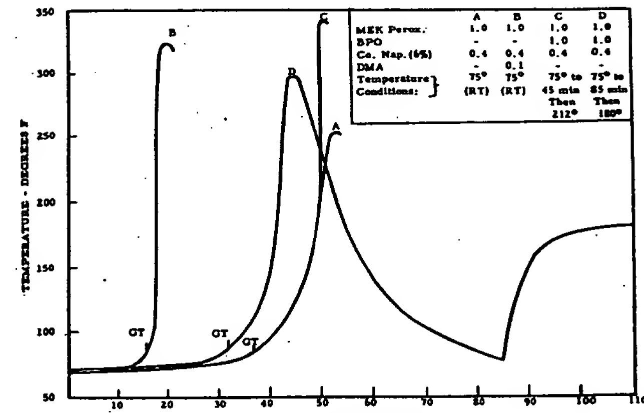


Figure II-1.5. Exotherm curves for room-temperature curing systems in polyester resins.

as a boat. By using a double-promoted system, the over-all mold time was reduced to 2½ hours because near-ultimate properties developed much more rapidly.

Curves *C* and *D* in Figure II-1.5 attempt to show additional methods by which closer-to-ultimate properties might be developed in a polyester hand lay-up structure. In Curve *C*, 1% BPO was mixed into the resin in addition to the MEK peroxide, and the sample placed in a 212°F bath at time of gelation. In Curve *D*, 1% BPO and 1% MEK peroxide in a standard polyester were gelled at room temperature under the influence of 0.4% cobalt naphthenate, and the sample was allowed to cure and pass through exotherm while maintaining ambient room-temperature conditions. Additional heat of a 180°F bath after the sample cooled to room temperature (85 minutes) did not initiate any further exothermic reaction in the resin due to the extra addition of the BPO. Conclusions: Additional catalyst or presence of a catalyst generally more reactive at elevated temperatures further advances a room-temperature cure by increasing the intensity of the exothermic reaction. However, once the resin has passed through the cure cycle, no secondary exotherm results if the resin is subjected to an elevated temperature (as for postcure). In actual practice, the degree of cure may be considerably advanced by postcuring at elevated temperatures.

In addition to making SPI gel-time test measurements, advancement of a cure prior to gelation may be observed by noting the viscosity increase of the resin. Following gelation, systematic time-interval Barcol gauge readings make possible a graphic or numerical tracking of the cure. After a laminate has been formed, existence or nonexistence of a complete cure may be determined by (a) measuring per cent retention of ultimate flexural strength after a two-hour boil in distilled water, and also by (b) making certain that no increase in flexural modulus of elasticity greater than 15% results when the laminate is subjected to a postcure of two hours at 180°F.* In the two-hour boil test, insufficient original cure is indicated by wet values in excess of the dry values, since heat from the boiling water advances the resin cure beyond its suspended state.

As previously indicated, promoters are also used for specific applications at intermediate and

elevated temperatures; however, their main usage is in the room-temperature and intermediate-temperature cure systems.

General characteristics to be desired in a promoter are: compatibility with, or solvency in a material compatible with polyester resins; low cost; lack of toxicity; and freedom from post-cure odor, discoloration, or interference with complete polymerization. Required promoter concentrations are usually determined empirically to suit specific systems, and range from 0.01 to 5.0%, with 0.05 to 0.1% optimum for the majority of promoters.

Table II-1.13 presents a listing of the comparative reactivity of seven of the more commonly used promoters, and (for comparison) one inhibitor, all at 0.2% concentration in each of eight specific peroxide catalysts.[illegible] In reporting the data of Noller, Stengel and Mageli, bath temperatures in which the exotherm curves were run are given, as well as kick-off temperatures, gel and cure times, and peak exotherm temperatures. The bath temperature used depended upon the type of peroxide and the additive being tested, and was also selected so as to show an inflection in the exotherm curve from which the kick-off temperature could be determined. In the instances where reported kick-off temperatures are below 180°F, the "kick-off" occurred before the sample reached bath temperature.

The basic unsaturated polyester used for all determinations was composed of 1.0 maleic anhydride, 1.0 phthalic anhydride, 2.2 propylene glycol, hydroquinone 0.013%, reacted to an acid number of 45-50, and seven parts of the reacted alkyd mixed with three parts of monomeric styrene.

A further summary of promoters cited in the literature, together with remarks indicative of their particular function or properties, is presented in Table II-1.14. This listing may be consulted as a general reference in planning use of a promoter-catalyst system for particular curing requirements.

Promoters are usually incorporated into the resin by the manufacturer to provide a balanced system with guaranteed uncatalyzed and catalyzed stability. A solution may be desirable for better dispersal. Mixing must be thorough to provide the necessary cured-state uniformity. Promoted and double-promoted resins usually have shorter storage lives and are more temperature-sensitive than unpromoted resins; hence, the explicit instructions of the manufacturer regarding catalysis and use of such resins should be rigidly observed. The variation in gel time with temperature and catalyst concentration for a typical rapid room-temperature curing resin is shown in Table II-1.15. Similar data may be developed for intermediate-temperature (150°F) cures.

On-the-job use of promoters is also common practice. Although more freedom is possible in the controlling of the amount to be added, precautions must be taken to guard against quality variations in the cured resin or laminate due to improper or insufficient mixing of the promoter. Several unique systems have been devised[illegible] in which a constant amount of solvent or compatible monomer containing the promoter (or catalyst) is added to each resin batch. The gel time may be maintained constant despite varying shop-temperature conditions by systematically or automatically varying the amount of promoter (or catalyst) contained in the solvent or monomer.

Apart from toxicity precautions, if and when called for, the cardinal rule governing use and handling of promoters is: *do not mix them directly with any catalyst materials outside the resin batch.* Almost all promoters act as powerful reducing agents and induce explosive reactions when placed in direct contact with peroxide catalyst materials.

APPLICATIONS

There are five major classifications of methods of processing Reinforced Plastics, simply listed as follows with subdivisions, and more fully described in Section IV, Molding Methods.

A. *Manual Molding Methods,* including hand lay-up, bag molding, spray-up, processing and lay-up use of prepreg material, contour weaving, sandwich construction, potting and encapsulation, putties, gel coats and other coatings, and emulsifiable binder resins. Medium- to slow-speed room-temperature curing systems apply with the exception of the prepreg and emulsion binder method.

B. *Matched-Die Molding Methods,* including mat and preform molding, premix molding, and injection and transfer processes. Rapid, elevated temperature curing systems are employed.

C. *Filament Winding Methods,* which comprise either wet or dry application of continuous filament fiber-glass reinforcement, or applica-

Text continued on p. 48.

TABLE II-1.13. COMPARATIVE EFFECTS OF COMMONLY USED PROMOTERS ON THE GEL AND CURE CHARACTERISTICS OF VARIOUS PEROXIDE CATALYSTS

		Control (no promoter added)	N-N-dimethyl p-toluidine	Dimethyl Aniline	Diethyl Aniline	Lauryl Mercaptan	Cobalt Naphthenate	Manganese Naphthenate	Hydroquinone
1. Benzoyl peroxide	Bath temp °F	180	180	180	180	180	180	180	240 (no results at 180 or 212)
	Kick-off temp °F	200	80	85	140	195	200	205	245
	Gel time, min	4.0	0.1	0.1	0.2	3.0	4.8	9.9	4.1
	Cure time, min	6.0	0.9	0.9	0.9	4.9	6.9	11.4	5.3
	Peak exo. temp °F	388	369	313	414	404	386	375	447
2. Acetyl peroxide	Bath temp °F	180	180	180	180	180	180	180	240
	Kick-off temp °F	195	140	160	180	190	200	200	210
	Gel time, min	1.5	0.2	0.5	1.4	2.3	9.8	11.9	1.6
	Cure time, min	2.5	1.1	1.4	2.6	3.9	11.6	13.7	2.8
	Peak exo. temp °F	385	391	384	422	412	386	390	441
3. Methyl ethyl ketone peroxide	Bath temp °F	180	180	180	180	180	180	180	266
	Kick-off temp °F	210	205	200	210	190	100	215	275
	Gel time, min	4.9	3.0	2.9	4.2	1.5	0.9	5.4	9.0
	Cure time, min	10.1	6.0	5.8	8.3	3.4	3.9	8.5	12.5
	Peak exo. temp °F	326	365	357	349	390	302	353	359
4. *t*-Butyl hydroperoxide	Bath temp °F	212	212	212	212	212	212	212	266
	Kick-off temp °F	270	240	240	250	240	250	260	295
	Gel time, min	11.0	3.6	3.6	5.1	3.8	5.5	7.6	22.9
	Cure time, min	19.8	5.8	6.0	8.4	6.0	9.7	13.0	25.0
	Peak exo. temp °F	288	410	394	426	436	374	359	468
5. Lauroyl peroxide	Bath temp °F	180	180	180	180	180	180	180	240 (no result at 180 or 212)
	Kick-off temp °F	180	130	160	190	180	180	190	190
	Gel time, min	1.5	0.2	0.5	0.2	3.0	4.8	9.9	4.1
	Cure time, min	2.5	1.4	1.7	0.9	4.9	6.9	11.4	5.8
	Peak exo. temp °F	385	370	347	414	404	386	375	447
6. Bis(1-hydroxycyclohexyl) Peroxide	Bath temp. °F	180	180	180	180	180	180	180	240
	Kick-off temp °F	220	230	230	230	200	100	250	280
	Gel time, min	9.2	23.7	3.7	15.8	2.6	2.7	21.5	9.3
	Cure time, min	11.1	23.7	15.5	24.8	5.5	9.5	28.8	19.5
	Peak exo. temp °F	315	243	226	243	379	226	285	325
7. *t*-Butyl perbenzoate	Bath temp °F	212	212	212	212	212	212	212	266
	Kick-off temp °F	245	230	230	235	165	215	250	280
	Gel time, min	8.9	3.3	3.6	4.0	0.5	3.6	10.6	7.5
	Cure time, min	12.0	4.6	5.2	5.7	1.3	4.9	13.6	9.2
	Peak exo. temp °F	392	432	409	430	430	412	400	466
8. Di-*t*-Butyl peroxide	Bath temp °F	240	240	240	240	240	240	240	290
	Kick-off temp °F	280	260	260	270	280	290	235	320
	Gel time, min	10.8	3.6	3.4	5.9	6.7	16.8	14.0	9.9
	Cure time, min	13.2	5.0	4.7	7.7	9.9	20.1	16.6	11.4
	Peak exo. temp °F	423	449	434	455	442	413	423	444

Table II-1.14. Function of Various Promoters Used with Polyester Resins

Promoter	Function and/or Remarks
Inorganic Compounds:	
1. Sulfur dioxide	Effective initiator for polyesters but are limited in application (gaseous).
2. Hydrogen sulfide	Same as No. 1.
3. Stannous chloride 4. Ferrous chloride	These and other multivalent metals in a low oxidation state behave as promoters. Other ferrous and stannous salts are also applicable.
5. Carbon black	Acts as inhibitor with organic peroxides alone, but acts as accessory promoter with peroxides plus conventional promoters.
6. Calcium hydroxide	Induces room temperature cure when used at 0.5 to 5% with some conventional organic peroxides. (Similar effects noted using oxides and hydroxides of barium, strontium, magnesium, and also calcium oxide.
7. Inorganic reducing agents	HCl, H_2SO_4 are effective as room-temperature promoters, but have no potency in high-temperature cures.
Organic Compounds:	
8. Cobalt naphthenate, 6%	Widely used (0.1–2.0%) as room-temperature-cure promoter with methyl ethyl ketone peroxide or cyclohexanone peroxide. Room-temperature systems using cobalt naphthenate as the sole promoter do not rapidly develop optimum properties as indicated by flexural[21] and wet-strength retention tests. An accessory promoter is desirable. Cobalt metal is also supplied in another more concentrated form (Cobalt HR-254, containing a chelating agent), which exhibits better uncatalysed stability (less gel-time drift) than cobalt naphthenate by supposedly releasing cobalt ions more gradually after having been incorporated into the polyester resin by the manufacturer. Both forms strongly color the resin and impart some tinting to the cured part; which can usually be masked with fillers or pigments. The cobalt metal present provides the true reaction with catalyst to release free radicals.
9. Dimethyl aniline	An aromatic amine widely used (0.05 to 0.2%) as an accessory room-temperature-cure promoter with cobalt naphthenate, and also as a room-temperature-cure initiator with BPO catalyst. DMA is cheap and effective for fast gel and cure, but is toxic, maladorous, and is generally not desirable in gel coats and resin structures to be exposed to sunlight and weather due to discoloration upon aging.
10. N,n-diethyl aniline	Generally requires a larger percentage content than DMA for an equivalent gel time, but provides a shorter cure time, hence produces a lower molecular-weight polymer which is not quite as strong. DEA has some advantage over DMA in producing less gel time drift on aging after the promoter is incorporated into the resin. DEA is also cheap but is toxic and will produce discoloration upon aging.
11. N,n-dimethyl-p-toluidine	Similar in performance to DMA and DEA and generally used in similar applications. This promoter discolors more slowly and to a slightly lesser degree, and is less toxic than DMA or DEA. However, it is more expensive and slightly slower or more sluggish in curing.
12. N-phenylethanolamine	Not commonly used.
13. 1,3-dibutylthiourea	Useful together with *t*-dodecyl mercaptan in promoting room-temperature gelation and curing using cumene hydroperoxide as catalyst.

Table II-1.14.—*Continued*

Promoter	Function and/or Remarks
14. N or *t*-dodecyl mercaptan 15. (Same as lauryl mercaptan)	Mercaptans provide a colorless promoter exhibiting no discoloration on aging, and reportedly prevent air-inhibition on curing when used with manganese naphthenate and *t*-butyl hydroperoxide. However, they actually produce gelation but do not cure by themselves, hence must be added only at the same time as the catalyst. Since the mercaptans gel the resin, and the catalysts cure, the two not actuating simultaneously or together, a low molecular and hence, low strength polymer results, cure being only about ¾ complete. Mercaptans also give erratic gel-time results when used as promoters in concentrations of less than 0.05%. They are maladorous and generally regarded as not being as effective for promoting as are the aromatic amines.
16. Triethylene diphosphite	Not commonly used.
17. Phosphoronitrilic chloride	Not commonly used.
18. Hydroquinone derivatives	2,5-diphenyl *p*-benzoquinone and others are inhibitors at room temperature in polyester resins, but show some activation effect when stored at elevated temperatures (110°F).[19, 22] Di-*t*.-butyl hydroquinone combines good room-temperature inhibition with minimum prolongation of cure at elevated temperatures. Hydroquinone derivatives are not in general use as promoters.
19. Ferric acetyl acetonate	Not commonly used.
20. Manganese naphthenate or octoate	Complete cure at room temperature is difficult as for cobalt naphthenate alone.
21. Stannous octoate	Discolors more strongly than cobalt naphthenate. No advantage over cobalt naphthenate.
22. Ferric octoate	No advantage over cobalt naphthenate. Discolors strongly.
23. Phenyl phosphinic acid	Shortens room temperature gel times of all peroxides except BPO and di-*t*.-butyl peroxide. Basis of other proprietary promoters.
24. N-butyl sulfite	Used at 2% in resins promoted with *t*-butyl hydroperoxide for faster cure at higher temperatures. Not commonly used.
25. Diphenyl hydroxyphosphine	Same as above. Not commonly used.
26. p-toluene sulfonic acid	Used 0.03 to 0.13%. More commonly used as a catalyst for the esterification reaction of alkyds.
27. 4,4-tetramethyl diamino diphenylmethane	Not commonly used.
28. 1,2-propylene diamine	Not commonly used.
29. N-ethyl-*m*-toluidine	Similar to dimethyl *p*-toluidine. Not commonly used.
30. Ascorbic acid and isoascorbic acid	Colorless promoters; valuable in intermediate temperature cure (architectural sheet); inconsistent in gel-time behavior. Not as effective as aromatic amines.
31. Dimethyl phosphine	Employed (0.15 to 0.5%) for fast room-temperature cure of excessively inhibited polyesters. Not commonly used.
32. Triethanolamine	Similar in performance to, but not as effective as DMA and DEA. Not commonly used.
33. Tri-isopropanol amine	Same as above. Not commonly used.
34. Meta-toluidine	Useful promoter but requires external heat for activation. Not commonly used.
35. Diethylenetriamine	Same as No. 34.
36. Piperidine	Same as No. 34.
37. Aldehyde amines	Need additional heating at higher temperatures than Nos. 34, 35, and 36 for complete cure. Not commonly used.
38. Sodium sulfonate or dioctyl succinate	Useful (0.01 to 1%) together with peroxide catalysts to obtain clarity in laminates. Not commonly used.
39. Methyl iodide	Methyl iodide (0.5–1.0%) stabilizes against discoloration caused by some peroxide catalysts, but laminate hardness is somewhat diminished. Not commonly used.

Table II-1.14.—*Continued*

Promoter	Function and/or Remarks
40. Quaternary ammonium compounds	Most quaternary ammonium chlorides are effective promoters, but some perform as inhibitors. The promoters may be effectively incorporated into the resin with stability, but produce discoloration. Several proprietary promoters are based on these compounds.
41. Hydrogen halides	Proprietary—similar in promoting effect to quaternary ammonium chlorides.
42. Cobalt linoleate	Room-temperature cure promoter with cyclohexanone peroxide or methyl ethyl ketone peroxide. The cobalt metal ions are the effective promoters, hence no advantage over cobalt naphthenate.
43. Propylene diamine	Not an aromatic amine. Not commonly used.
44. Tetraethylene pentamine	Not commonly used.
45. Mercapto ethanol	Similar to *t*-dodecyl mercaptan. Not commonly used.
Miscellaneous Promoters:	
46. Ultraviolet radiation	Free radicals are produced in polyesters by action of artificial ultraviolet excitation (3000 Å), also by exposure to sunlight. Both will promote cure in polyesters sensitized with benzil (5%) or benzoin (5%). Benzil is more stable and provides long pot life; benzoin is more reactive and is preferred. Both provide gel times of thirty minutes after exposure starts, even at 32°F. No peroxide catalyst is required, but may be used (BPO preferred). The total amount of sensitizer may be mixed into the resin with exceptional uncatalyzed stability (in dark), precluding small-batch mixing. However, gelation is not uniform throughout a structure as in peroxide-catalyzed systems. This is advantageous in types of molding such as rod stock where it would be desirable to produce a surface cure which would maintain shape, after which the internal portion could be heat-cured. Neither benzil nor benzoin contribute to good light stability.
47. Ambient humidity	Per cent relative humidity reportedly acts to affect room-temperature cures together with temperature and activator concentration variables. Water acts as a good inhibitor, but only a very small percentage can be tolerated due to its deleterious effect on cured resin properties.

TABLE II-1.15. VARIATION IN GEL TIME WITH TEMPERATURE AND CATALYST CONCENTRATION FOR A TYPICAL RAPID ROOM-TEMPERATURE CURING POLYESTER RESIN

Temperature °F	Gel Time in Minutes for the Indicated Concentrations of MEK Peroxide Catalyst		
	0.5%	0.75%	1.0%
60	89	51	35
78	48	30	18
90	25	18	10

Data: Courtesy Allied Chemical Corp.

tion of prepreg materials to a rotating form. High-temperature oven cures are employed.

D. *Extrusion methods*, including solid rod stock, hollow tubing and piping, structural cross-section extruded shapes, continuous laminating solid, impregnated stock or of mat-type products. Rapid and medium-speed high-temperature cures apply.

E. *Centrifugal Molding Methods*, including large diameter (>2 in.) pipe, tanks, and cylinders. Rapid- and medium-speed high-temperature curing systems are used.

In addition, general characteristics which improve handling properties and processing techniques, contributing in a minor or at least a secondary way to end-product properties, may be obtained by adding or "cooking in" special additives. Such properties as viscosity, thixotropy, high hot strength, high or low exotherm, extended pot life, freedom from surface tackiness (air inhibition) on curing, low shrinkage,

resistance to crazing, rigidity or resiliency (affecting mechanical properties), surface gloss and hardness, are among those obtainable.

However, there are five specific classes of polyester resins which have been developed with widely divergent properties to satisfy the performance requirements of the fields in which they are called upon to serve as components of RP. These five resin types have individually resulted from the best-known combinations of resin ingredients (Table II-1.5), monomers (Table II-1.6) and curing systems to produce the desired qualities. As long as the salient end properties of the resin are maintained, any of the molding methods may be resorted to, and any of the handling and processing-improvement characteristics may be incorporated. The boundaries of resin-type performance are not firm lines of demarcation, i.e., high heat-deflection temperature resins may also show superior chemical durability.

Brief descriptions of the five major classes follow:

General Purpose

These multipurpose resins make possible the good electrical and mechanical properties for which polyesters are noted, augmented of course by the reinforcement. They may be either rigid or resilient, filled or colored, and are used for general, nontranslucent, decorative molded items. They also possess average-to-good chemical resistance, and, of course, may be infinitely modified to suit the great variety of molding processes and curing cycles. They will show discoloration, loss of gloss, and fiber blooming upon weathering, have a maximum long-term peak, continuous-exposure temperature of 250°F. Electrical resistance is good and may be further improved by incorporating diallyl phthalate monomer, but cure time and amount of catalyst required are correspondingly increased.

Light-Stable and Weather-Resistant Resins

These resins are manufactured to possess high clarity and freedom from any amber discoloration due to processing (APHA = 20 to 150), low viscosity (1.5–3.0 poise) for rapid wet-out of reinforcement, rigidity, and high reactivity for rapid cure, and also high surface gloss and hardness. They usually contain a mixture of styrene and methylmethacrylate or methylacrylate monomers to provide freedom from surface erosion and fiber blooming on weathering, and also contain stabilizers to resist yellowing or darkening due to action of ultraviolet rays in sunlight (phenyl salicylate and ortho-hydroxybenzophenone derivatives are typical stabilizers). Creation of a resin-rich surface layer provides good insurance against surface erosion and fiber blooming. Polyester gel coats prevent fiber erosion during long and continuous outdoor exposure, but are subject to crazing. Laminates made from transparent light-stable resins withstand approximately four years in a temperate climate (less in semitropical climates), prior to serious fiber blooming. The eroded laminates may be rejuvenated with applications of clear lacquers. Recent developments have made possible application of a weather-resistant film on the laminate surfaces during manufacture; the film remains an integral part of the laminate.

While not completely transparent, the light-stable and weather-resistant resins (hence, laminates) may be tinted and used in home or industrial structural glazing, as interior decorative panels. These panels are strong, light in weight, shatterproof, and are enjoying acceptance and increasing annual production as an outstanding application of RP.

Chemical-Resistant Polyester Resins

Utilization of chemical-resistant polyester resins to supersede metal structures which are inexorably subject to rust and corrosion is only in its infancy. Large-scale structures (filament winding and hand lay-up) predominate (tanks, ducts, hoods, piping, etc.), but high-temperature matched-die molded preform and premix parts are also in wide usage.

The main cause of chemical attack of resins in an aqueous environment is hydrolysis, which results in chemical decomposition due to attack and resultant rupture of the ester linkages in the polymer chain. Chemical-resistant resins have been designed so that ether linkages replace a percentage of the ester linkages by reacting fumaric acid and a bisphenol A intermediate, and adding styrene monomer. Establishment of more of a ring structure than that found in a general-purpose polyester results. The higher molecular weight of such a resin also contributes to the resistance to hydrolysis.

Polyester resins with increased chemical durability and thermal stability, improved strength properties, which also permit blending with

higher proportions of styrene have resulted by reacting isophthalic acid—based formulations to higher molecular weights.[a]

Resistance to chemical attack in polyesters has also been achieved by using hydrogenated bisphenol A with maleic, fumaric, and phthalic acids and propylene glycol.[a] The most chemical-resistant of a series of resins had a high heat-deflection temperature, low density, higher viscosity, absence of tack in curing, low curing shrinkage, and good adhesion to the glass reinforcement, all of which contributed to resistance to hydrolysis. A resin-rich surface also favors resistance to chemical attack.

Chemical durability in polyester resins and end-use laminates is evaluated by visual observation after exposure, by determination of actual weight loss or gain, and also by determining per cent retention of physical properties. The actual outcome of durability evaluation depends upon the chemical to which exposure is made, and upon time of exposure. Retention of up to 90% of original strength in 25% acid concentrations and up to 60% in 5% strong-alkali concentrations is possible.

Resins with High Heat Deflection Temperature

The use of maleimide and triallyl cyanurate (potential functionalities of 4 and 6, respectively) as monomers with optimum polyester (alkyd) formulations has resulted in resins and hence laminate structures with 50% retention of original strength when maintained and tested at 500°F. A stringent curing cycle is required, and the material is toxic and expensive. However, the 500°F limit coupled with ease of polyester handling provides a material which cannot be produced in any other way. Aircraft and missile research continues to demand materials which have the high strength, comparatively low moduli and shatterproof properties of RP, yet which will withstand creep and thermal disintegration at high temperatures.[a, a]

Flame-Resistant Resins

These are also referred to as fire-retardant and self-extinguishing resins. Addition of chlorine, saturated and unsaturated acids, minimum amounts of monomer, and specific compounds such as antimony trioxide have enabled these resins, when made into structural panels, to gain very low flame-spread ratings (ASTM D635 and D747), and also values as low as 21 to 25 in the National Fire Underwriters' Tunnel Test. However, when subjected to the Columbia Fire Test[a] or equivalent, they generate great volumes of black smoke and noxious fumes. They are not self-extinguishing but ignitable, which indicates the persistent limitations of the so-called self-extinguishing resins.

Large quantities of flame-resistant resins are used either for blending or full strength to reduce fire ratings to self-extinguishing for some building panels, electrical components and fuel tanks. However, the innate characteristic of being a combustible organic chemical precludes building code approval as an interior construction material required to provide highest fireproof ratings. It also eliminates these materials from such uses as ablation shields.

The major markets or areas in which Reinforced Plastics are essentially used[a] are of interest: (1) aircraft and missiles, (2) appliances, (3) boats, (4) construction, (5) consumer products, (6) containers, trays and industrial housings, (7) electrical, (8) pipes, tanks and ducts, (9) transportation, and (10) miscellaneous uses. Polyester resins of course represent the largest resin volume for RP with phenolics and epoxies next in order, with specialty resin types being channeled into the extraordinary applications.

Solid polyesters result when addition of monomer to the reacted base resin formulation is withheld, and the material is permitted to cool to room temperature directly from the reactor. The only requirement is that the base formulation be high enough in viscosity at normal room temperature to preclude softening and coalescence after the resin has been pulverized. Additions of stearates (1 to 1.5%) are made to prevent this blocking.

Actually, any resin composition satisfying the viscosity requirements may be marketed as a powdered polyester. General-purpose and chemical-resistant types are most widely used, and the major application is as a binder material for fiber-glass chopped-strand and other mat products. The solubility of the base resins in styrene is particularly important in these binder resins. Mat products which are to be used for hand lay-up and corrugated sheet manufacture require fast wet-out and rapid solution of the binder material in the laminating resin, while those for matched-die molding processes require a low-solubility binder which resists washing. Powdered mat-binder resins may or may not require catalysts.

Molding compound formulations and some prepreg operations may be built around use of powdered polyesters. Bulk solid resins are used in other prepreg processes. Some means of cross-linking is of course required if ultimate resin properties are to be developed in these monomer-free resins.

APPENDIX II-1.1: SPI PROCEDURE FOR RUNNING EXOTHERM CURVES—POLYESTER RESINS

1. Scope

This method is designated for use in determining the "exotherm curve" of an uncured polyester resin, and covers the "Standard 180°F Exotherm Curve," other standard exotherm curves, and certain variances which may be required for special resins or to supply information which is important for specific applications.

2. Test Sample

Liquid, uncured, uncatalyzed polyester resin, essentially at room temperature. A minimum of 80 grams of resin is required for both exotherm curve and catalyzed stability. 20 grams of resin will suffice for the exotherm curve only.

3. Apparatus and Materials

a) Recording Pyrometer* 0 to 500°F range Iron Constantan, 30 inches per hour chart speed.
b) Constant-temperature water bath, controlled to 180°F + 0.2°F, water capacity = 6 gallons, stirrer agitator, provided with rack to hold test tubes immersed in the water to within one-half inch of the top of the test tube.
c) New, clean test tubes, soft glass with lip, 19 × 150 mm.†
d) Iron Constantan wire, 24 B & S gauge.
e) Triple-beam scale with capacity of at least 200 g, and sensitivity of 0.01 grams.
f) Benzoyl peroxide 99% purified.‡
g) Vented-cork stoppers for test tubes.
h) 4-ounce jar (wide mouth), spatula, test tube rack, pliers.

4. Procedure

a) Preparation of Catalyzed Resin.

Weigh 0.80 grams of benzoyl peroxide 99% purified into a 4-ounce, wide-mouth jar. Add 80 grams of the resin to be tested and mix thoroughly. Be careful to mix as little air as possible into the resin. Pour 10 (±) grams into each of two of the 19 × 150 mm test tubes, insert cork stoppers and let stand for 25 (±10) minutes, away from heat and strong light. The remaining resin may be used for additional curves if necessary, or for catalyzed stability test.

b) Preparation of Thermocouple

The iron and constantan wires should be long enough to reach easily from terminal posts of the instrument to the bottom of the test tube when it is in place in the bath. The wires must be clean and free of kinks. Straighten the wires, and polish the ends with emery cloth if they are not bright. Hold the ends in a pair of pliers so that they protrude together, in the same direction, about one inch.

While holding the wires firmly in the pliers, spread the ends apart and twist them together with the fingers ten times (five complete turns) to form a snug, uniform, twisted portion about one-half inch long. This twisted portion is the part of the thermocouple which actually measures the temperature of the sample and to get a good curve there must be good, tight contact between the two wires in the twist, and the twist must be located in the center of the resin sample. If the two wires touch each other at any point other than at the twisted part (either above or below) the curve will not be correct.

Bend the wires above and below the twist so that when the thermocouple (twisted portion of the wires) is slipped into the test tube, the twisted part will be guided to the center of the tube. Do not let these ends touch each other. (See Figure II-1.6.)

c) Running the Curve

When 25 (±10) minutes have elapsed from the time the resin was catalyzed, slide the twisted thermocouple wires into one of the test tubes containing 10 grams of catalyzed resin, so that the thermocouple is centered in the resin sample in all directions. Insert the test tube in the rack as far as it will go, and start pyrometer. Check all thermocouple wires to make sure that they are not touching each other anywhere except at the twisted portion. Let the pyrometer run for at least two minutes after the curve reaches its peak. Remove the tube from the bath, the plug from the tube and cut the wires just above the plug. Observe the plug for abnormalities such as blowing (bubbles), incomplete cure, unusual color, etc. If normal, discard plug and tube.

Run curves in duplicate. If they do not agree, run enough additional curves to produce reliable results.

* Leeds & Northrup Speedomax (Type G) with chart #206, or equivalent.
† Kimble 45050 Class 2, or equivalent.
‡ Material is commercially available.

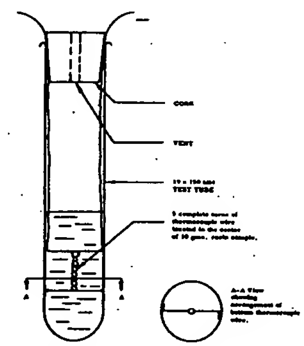


Figure II-16. Sketch of thermocouple in test tube.

5. Report

Measure and record the following information from those curves which are considered reliable.

A. Time from 150°F to bath temperature.
B. Time from 150°F to 10°F above bath temperature.
C. Time from 150°F to peak.
D. Peak temperature.

6. Variances

a) Bath temperature and fluid: test may specify a different bath temperature and/or fluid (125°F, room temperature, etc., oil, etc.) Test may specify Room Temperature Curve without the use of a bath (usually 50 gram sample in paper cup at existing ambient temperature). Unless otherwise specified, use water at 180°F.

b) Catalyst: Test may specify different catalyst and/or a different catalyst concentration. Unless otherwise specified use 1% benzoyl peroxide 99% purified.

c) Sample size: Test may specify a larger or smaller sample and a different vessel (different-size test tube, beaker, or paper cup). Unless otherwise specified use a 10 gram sample in a 19 × 150 mm test tube.

d) Thermocouple wires: Test may specify 30 B & S gauge wires, particularly for very small samples, or a ⅛ inch thermocouple needle. Unless otherwise specified, use 24 B & S gauge wires.

e) Chart speed: Where cure time is very long, test may specify a slower chart speed, e.g., six inches per hour. Where cure time is very short, test may specify a faster chart speed, e.g., 120 inches per hour.

f) Procedure: Waiting period may be shortened or omitted for specific systems.

7. Standard Exotherm Curves

a) Certain commonly used combinations of these variances, other than those specified for the "Standard 180°F Exotherm Curve," are accepted as standard procedures. These are listed below. Other commonly used combinations may, from time to time, be designated as standard procedures, and added to those listed.

	Standard 180°F Exotherm Curve	Standard 300°F Exotherm Curve
a) Bath fluid Bath temperature	Water 180°F	Mineral Oil* 300°F
b) Catalyst	1% BPO 99% Purified	1% BPO 99% Purified
c) Sample size and vessel	10 gm 19 × 150 mm test tube	20 gm 19 × 150 mm test tube
d) Wire size	24 B & S gauge	24 B & S gauge
e) Chart speed	30 in. per hour	120 in. per hour

* Standard Oil Company's Sohivis J 53 or equivalent (Flash point 445°F).

References

No.	Author(s)	Title or Periodical	Vol.	P.-Sect.	Year
1	Mitchell, J., Jr. Kolthoff, I. M. Broskauer, E. S. Weissberger, A.	"Organalysis," Vol. 1, New York, Interscience Publishers, Inc.	—	11	1953
2	Lascoe, O. D.	Research Report No. 16, Purdue University, Lafayette, Ind.	—	—	Nov. 15, 1958
3	Anon	SPI-R.P. Div. Preprint	16	Follows bibliography p. 13	1961

No.	Author(s)	Title or Periodical	Vol.	P.-Sect.	Year
4	Bjorksten, J.	SPI-R.P. Div. Preprint	13	1-A	1958
5	Johnson, G. B. Meader, A. L. Perizzolo, C. F.	SPI-R.P. Div. Preprint	14	17-A	1959
6	Cass, R. A. Reaville, E. T.	SPI-R.P. Div. Preprint	15	5-A	1960
7	Skeist, I.	SPI-R.P. Div. Preprint	12	15-A	1957
8	Lowry, J. R. Smith, A. L.	SPI-R.P. Div. Preprint	11	17-C	1956
9	Morgan, P. A.	"Glass Reinforced Plastics," London, Iliffe & Sons, Ltd.	—	38, 41	1957
10	Lawrence, J.	"Polyester Resins" New York, Reinhold Publishing Corp.	—	—	1960
11	Bjorksten, J. et. Al.	"Polyesters and Their Applications," New York, Reinhold Publishing Corp.	—	—	1956
12	Nelb, R. G.	WADC Rev. of Structural Plastics	—	1	Sept., 1958
13	Barnes, R. S. Bourbeau, C. F. Cass, R. A. Palmer, J. F. Jr.	"Polyester Raw Materials Study," Monsanto Chemical Co.	—	—	Rec'd: Jan. 19, 1962
	See also: May, C. A., Mika, T. F. and Tess, R. W.	Modern Plastics	39 (No. 7)	144	1962
14	Anon.	"Composition and Utilization of Polyesters," Allied Chemical Corp.	—	35	1954
15	Kiehnle, R. H.	General Electric Co.	—	—	1927
16	Lawrence, J. R.	Personal Communication, Glidden Co.	—	—	July 16, 1962
17	Atlas, S. M. Mark, H. F.	Intern. Sci. & Technol.	Prototype	44	1961
18	Golding, B.	"Polymers and Resins," Princeton, N. J., D. Van Nostrand Co.	—	312	1959
19	Burnett, R. E. Cass, W. E.	Ind. & Eng. Chem.	46, No. 8	1619	1954
20	Bockstahler, T. E. Brown, C. A. Feuer, S. S. Rosenthal, I.	Ind. & Eng. Chem.	46, No. 8	1643	1954
21	Moffett, E. W.	Ind. & Eng. Chem.	46, No. 8	1615	1954
22	Sias, C. B.	Private Communication, Pittsburgh Plate Glass Co.	—	—	Apr. 5, 1962
23	Kline, G. M.	"Analytical Chemistry of Polymers, Part I"	18	549	1959
24	Riddle	"Monomeric Acrylic Esters," New York, Reinhold Publishing Corp.	—	—	1954
25	Stone, M. C.	SPE Jo.	—	—	Oct., 1960
26	Anon.	Tech. Bulletin No. 3-301, Miles Chemical Co.	—	—	—

Chapter II-2

PHENOL-FORMALDEHYDE RESINS

Although the reaction between phenols and aldehydes has been known since 1872, the chemist Leo Baekeland, through the period 1905–1909, systematically combined the reactants on an organized mole basis and actually became the first to establish commercial uses for the phenol-formaldehyde resinous product.

Baekeland solved the then major problem of evolution of volatiles during cure by introducing pressure molding. He also compounded the original plastic molding compounds by adding fillers to phenolic resins to reduce their brittleness after molding. He presaged and laid the groundwork for the present Reinforced Plastics industry by using phenolic resins in liquid form to impregnate paper and fabric, which were dried and ultimately press-cured, making possible both industrial and decorative laminates.

Fortuitously, the development of phenol-formaldehyde resin technology co-dated the expanding use of electric power in America. Because of their desirable electrical insulating properties and ease of molding, phenolics were placed in service to satisfy numerous industrial and domestic electrical requirements.

PHENOL-FORMALDEHYDE RESIN MANUFACTURE

Essentially, any of the compounds classed as phenols may be reacted with any aldehyde to yield a resin of the phenol-formaldehyde type (also known as phenoplasts or phenolplasts). However, phenol (C_6H_5OH, alias carbolic acid, phenylic acid, or hydroxybenzene) and formaldehyde (HCHO, alias oxymethylene, formalin, or formic aldehyde) constitute respectively 75 and 90% of all present phenolic synthetic resin production. Phenol is commercially desirable because of its high purity and lower cost, and formaldehyde because of its freedom from self-resinification.

Table II-2.1 illustrates graphically the two major classes of phenolic resins as distinguished by differences in processing.* Characteristic end uses are included for later reference.

The raw materials are processed using a specific type of jacketed reactor. The phenolic reactor is similar to that used to manufacture polyesters with exclusion of the thinning kettle, and addition of a larger-capacity reflux condenser for cooling and control purposes. Following is a general step-by-step description of the batch-process kettle operation:

(1) Phenol-formaldehyde and catalyst are charged and the mix temperature raised to 140 to 190°F accompanied by adequate agitation. Resoles remain as a continuous phase during reaction, while novolaks separate into two phases between which contact must be maintained by the agitation.

(2) Exothermic heat is generated when the reaction gets under way, and must be dissipated by refluxing under vacuum or by cooling-water coils inside the kettle.

(3) The reaction is carried to the stage at which from 50 to as much as 99% of the formaldehyde has been converted. This is determined by continually testing for free formaldehyde (see appendix to this chapter). The amount of free formaldehyde allowed to remain is governed by the contemplated end use. Viscosity is also controlled by the degree of reaction and increases as polymerization progresses.

(4) Water is removed by vacuum distillation (40-90°C) from the resoles, to which alcohol is to be added, and from the novolaks, which are to become solid resins and in which melting points must be controlled. These latter resins must be as free as possible of volatiles. Water is

TABLE II-2.1. PHENOLIC RESIN TYPES

Classification	One-Step (Resole)		Two-Step (Novolak)
Composition ratio	Phenol = 1.0 Mol to Formaldehyde = 0.9 Mol or more A	B	Phenol = 1.0 Mol to Formaldehyde = 0.9 Mol or less
Reaction catalyst	*Strong Bases*, i.e., NaOH, CaOH, KOH, quaternary ammonium compounds, and combinations; quantity required = 0.5 to 15% of phenol charge. Catalyst neutralized with mineral acid in some cases.	*Weak Bases*, i.e., NH_3, primary, secondary, and tertiary amines and combinations; quantity required = 0.5 to 6% of phenol charge.	*Acids*, i.e., formic, sulfuric, phosphoric, oxalic, trichloroacetic, etc.; quantity required = 0.1 to 2% of phenol charge; is sometimes neutralized to form a salt which may precipitate out of the resin.
Method of handling and characteristic form of the reacted resin	Removed from reactor and cooled; maintained as a liquid.	Condensation water vacuum-distilled off; redissolved in alcohol for most uses.	Condensation water vacuum-distilled off; removed from reactor and solidifies when cooled; ground to fine powder or left in lumps; resin may be redissolved if necessary.
General properties (uncured state)	Water-soluble; dilutability = 100 parts water to 1 part resin. Sp. gr. = 1.01–1.25; solids are thermosetting.	Slightly soluble in water; maximum dilutability = 20 parts water to 100 parts resin (varnishes). Sp. gr. = approximately 1.15 (in alcohol); solids are thermosetting.	Solids are thermoplastic (melting point = 175–300°F); resins are too brittle at room temperature for any reliable applications in this intermediate stage.
Stability	Unstable; must be refrigerated prior to use to delay advance of final condensation polymerization.	Unstable; must be refrigerated prior to use.	Stable; some compositions have maximum shelf life of one week at 320°F.
Curing requirements and behavior	Cures by heat or change of pH or both; acidic catalysts may be added.	Cures by heat and low pressure, or change of pH; acid catalysts may be added; partial precuring is possible.	Requires addition of 10-15% hexamethylene tetramine, formaldehyde, or other methylol-group donor to bring methylol ratio up to that of resoles for cure; becomes thermosetting upon application of heat and high pressure.
Typical uses	Binders, coatings and casting.	Industrial and decorative laminates, adhesives.	Molding compounds, coated foundry sand, and brake-lining binders.

generally permitted to remain in the strong-alkali resoles, but the total amount of residual water is varied depending upon the end-use requirements.

(5) Liquid resins are cooled and pumped to storage or shipping containers. The novolaks are dropped to solidify in pans or onto a clean floor. They must be cooled rapidly to retain the melting point at the determined value, and are broken up into either pulverized, flaked, granulated, or other solid forms. To produce liquid novolak resins, reaction products are redissolved in alcohol or other solvent prior to removal from the kettle.

Note: The condensation reaction is brought as near to completion as possible in the kettle processing. To prevent further advance of cross-linking prior to ultimate use, one-step phenolics must be refrigerated, but two-step phenolics will exist at room temperature even after hexamethylenetetramine is added. In final cure, an additional, but probably slight exotherm occurs as the ultimate rigid condensation polymer is formed.

A normal phenolic kettle reaction requires from four to twelve hours for completion. Process variations consist of reacting in pressure vessels or by a continuous process, making possible greatly reduced reaction time. These variations are suitable only to specific resin types, however.

The chemistry of phenol-formaldehyde resins is described as (a) little understood and (b) as a complex combination of condensation and addition polymerizations and rearrangement of groupings, all of which may occur simultaneously.[3] Excellent anlyses of these reactions have been published, nevertheless,[4, 23, 29] and these may be summarized as follows:

In formation of resoles, the steps which occur in order are:

(1) Methylolation, or entry of methylol (CH_2OH) groups into the phenol ring in the ortho or para positions.

(2) Condensation of two methylol groups to form an ether bridge.

(3) Condensation between a methylol group and a phenol nucleus to form a methylene bridge (—CH_2—).

(4) Decomposition of ether bridges (—O—) to form methylene bridges and formaldehyde which immediately reacts via the first three reactions.

In the case of two-step resins:

(1) One molecule of formaldehyde plus two phenol nuclei will condense to form a methylene bridge (again in ortho or para position) with elimination of water.

(2) In order to cure the novolak, which *per se* is permanently fusible (thermoplastic), it must be further reacted with a material such as hexamethylenetetramine or formaldehyde. These furnish additional methylene bridges so that the novolak ultimately becomes a rigid cross-linked thermoset via the final process described for resoles.

The physicochemical state of phenolic resins during cure may be further described by defining three distinct progressions:[29]

A-Stage resin (resole): The initial condensation product (not cross-linked).

B-Stage resin (resitol): Cross-linking has commenced and the resin is thermoplastic, softening when hot and remaining hard and brittle at room temperature.

C-Stage resin (resite): The final polymerization stage has been reached and the resin is completely thermoset (insoluble and infusible).

Substitutions and Modifications

The many combinations of phenol and formaldehyde with various catalysts and curing conditions make possible a wide range of property variations in the finished thermoset resins. However, many substitutions are possible that improve the resins or eliminate nondesirable properties.

A large number of phenol-related materials can be directly substituted for phenol.[5] The property variation induced depends upon functionality, side-chain length, and other factors. A high degree of reactivity is desirable, as exemplified for instance by diphenolic acid which possesses eight reactive sites.

Commercial substitutes for formaldehyde are limited to paraformaldehyde and furfural (see Chapter II-4), but, as stated, formaldehyde is used in 95% of all phenolics produced.

Modifications include variations in kettle cycle as well as changes in mole ratio, catalyst type and concentration. Equally important, however, are the complex and simple inorganic or organic compounds added to the batch to induce improvements in moisture or chemical resistance, flexibility or other specific properties. These modifiers represent a group whose effects are determined empirically, usually without predetermined know-how, and their identification is in most instances kept confidential and proprietary.

To further provide interesting property variations, blends (alloys), and mixtures of phenolic resins with other polymer types such as epoxies and rubber (both thermosetting and thermoplastic) have been made. These have made possible improved adhesion of resins to various substrates or reinforcements, and also have produced compounds with greater abrasion and wear resistance.

TESTING

In addition to tests for water (or solids) content (titration or dehydration methods), viscosity, specific gravity, etc. commonly used or described previously (Chapter II-1), several other tests which are especially applicable to phenolics have been devised. These comprise the following: free formaldehyde, nonvolatile matter (two), stroke cure, set time, water dilutability (or tolerance). Procedures for these tests are duplicated in Appendices II-2.1 to II-2.6 at the end of this chapter.[29]

PHENOLICS AS REINFORCED PLASTICS

Phenolic resins find application as adhesives, bonding and impregnating agents, molding compounds and laminates, in coating operations, and cast products. The bonding, molding compound and laminating applications are of essential importance as Reinforced Plastics and will be discussed in detail.

In the general handling and curing, and in consideration of cured properties, certain advantages and disadvantages of phenolics compared to polyesters present themselves. These may be summarized as follows:[4, 5, 6, 8, 29]

Advantages

(1) Phenolics may be B-staged, permitting delayed cures. Only the more expensive DAP polyesters may be B-staged.

(2) General-purpose phenolics are 10 to 25% cheaper than polyesters on a solids basis.

(3) Phenolics possess higher temperature end points than polyesters, and retain a higher percentage of original strength after long-term high-temperature exposure.

(4) Phenolics may be especially formulated so as to provide excellent flame resistance, far superior to that for polyesters.

(5) They exhibit good mechanical properties, and good chemical and moisture resistance.

(6) They may be cured by heat and pressure alone and do not require complex inhibitor, promoter and catalyst additions.

(7) Solubility in water or water and alcohol of some phenolic types permits simplified handling.

(8) Phenolic resins have high hot-strength, minimizing tendency for warpage upon removal from molds.

(9) Cured phenolic resin solids are lower in specific gravity[29] than those for polyester resins.

Disadvantages

(1) Phenolics have innate qualities of extreme brittleness. Attempts to plasticize phenolics (as with water-soluble glycols) to build in resiliency equivalent to that obtainable in polyesters results in degradation of cured properties.

(2) Color problems are basic with phenolics. If the dark brown color of phenolics is avoided by processing in nickel kettles rather than iron or steel, the brown color develops on curing, probably due to quinoids and chromophores which result from oxidation. Phenolics cannot compete colorwise with polyester, melamine, or urea resins.

(3) Phenolics require higher pressures for cure in almost all molding or laminating operations due to necessity of counteracting forces caused by escaping volatiles. Only phenolic-glass laminates are molded at lower pressures.

(4) Phenolics cure at a slower rate than polyesters. Only finished resoles to which acid is added or resorcinol-formaldehyde resins will cure at room temperature, and these require further postcuring at elevated temperature to develop ultimate properties.

(5) Phenolics must be stored at temperatures below room temperature, and have maximum shelf lives of approximately 90 days (liquid). Powdered two-step resins to which hexamethylenetetramine has been added may be maintained at room temperature for extended periods, but tend to agglomerate to some extent.

(6) Upon outdoor weathering, phenolic-glass laminates warp, fade, and darken further. However, during weathering they erode less than polyester panels.[29]

Bonding

Phenolic resin has been used as a binder for fiber-glass and mineral wool insulation batting for many years. A strong-base type resole is usually used by mixing into a water-based formulation together with strongly alkaline emulsion extenders and stabilizers. The formulated resinous binder is spray-applied onto blown glass or wool fiber immediately after fiber-forming. The impregnated wool is collected on a moving belt which passes through a circulating-air oven in which the mat or batting is advanced through the B-stage and ultimately cured. Oven temperatures range from 325 to 450°F and the time required for curing depends upon the density and thickness of the mat to be produced. Corollary products are: industrial acoustical insulation made from finer fiber diameter (see Section III), flotation wool (phenolic-silicone binder), and compressed, higher-density decorative and insulation board.

Production of the compressed insulation board employs a unique process adaptation in which fiber-glass insulation-type matting with phenolic resin applied passes through the forming stage only, and is rolled up prior to curing the resin. Hence, the resin remains in the B-stage and two or three months' shelf life is normal if storage in excess of room temperature is avoided.

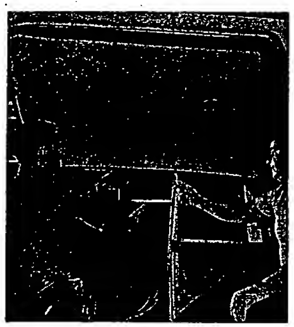


Figure II-2.1. Installation of automotive head-liner made from phenolic-bonded compressed fiber-glass insulation board. (*Courtesy American Motors Corporation and Johns-Manville Fiber Glass Division*)

The compressed board is ultimately processed to a finished product by molding to predetermined thickness stops as a laminate in a heated flat-platen or contoured press mold. Densities after molding vary from five to ten pounds per cubic foot as compared to maximum densities of only three pounds per cubic foot for the fine-fiber glass wool and fifteen pounds for mineral wool insulation.

Molding temperatures are maintained in the vicinity of 450°F so that more rapid cures are possible. Distillation of the resin is minimized due to the closed mold.

Originally (1951) the cured compressed board was channeled into products which utilized its properties of resiliency and vibration damping. Five-inch diameter rocket burnout rings and automotive protective dash panels were manufactured in quantity during the period 1951 to 1956. Subsequently, concentrated development resulted in a composite panel consisting of a decorative fiber glass fabric applied to the compressed board. Both the fabric and the B-staged resin-wool combination are laid up and cured together in a contoured press mold. A thin film of thermoplastic material is interleaved and softens during the molding cycle, bonding the glass fabric to the surface of the compressed board.

A unitized, one-piece automotive head-liner and a decorative acoustical ceiling panel represent the first major-volume items utilizing this compressed-board process. Figures II-2.1 and II-2.2 illustrate, respectively, the automotive head-liner and the acoustical ceiling panel. Sound-deadening qualities of the ceiling panel compared with other standard acoustical ceiling tile may be summarized by stating that the fiber-glass compressed board provides equivalent acoustical noise reduction, yet it weighs only one-tenth as much as standard panels.

Additional applications involving the bonding characteristics of phenolic resins comprise use in abrasives, friction materials, foundry sand cores and molds, impregnant for fiber-glass mat used in battery separators, and other miscellaneous uses.

Molding Compounds

In the present state of the art, resin manufacturers or intermediate processors supply, ready to mold, the major portion of all phenolic molding compounds used. The compounds are delivered to the molder in any of the four following forms:* granular powders, random resin-coated fibers (nodules), chopped or macerated resin-coated fabric, and resin plus fillers plasticized with solvents. In addition, molding compounds are further classified as low reinforcement types (or powder-molding compounds containing filler only), or as high reinforcement types containing high ratios of inorganic or organic material to resin. Methods of compounding include use of differential rolls, mixers, extruders and choppers. Eighteen distinct phenolic molding compound types (based on performance) are designated in ASTM Standard D700, and their minimum physical and electrical property values are also outlined. The several property types of molded phenolic materials which more or less define end usage comprise: general-purpose, impact (medium or high), electrical grade, heat-resistant, minimum bleed and odor, and special-property componds. Novolaks are usually used for powdered-type molding compounds, but resoles may be employed for the impregnated-fiber-type compounds.

Actual procedures involved in final-stage processing (curing) of phenolic molding compounds are briefly described as follows:

Preforming may or may not be necessary, as molding compounds can be fed to the cavity as powders. Random fiber or macerated cloth types may be preformed roughly by hand or by a tableting or pilling machine. Transfer molding usually requires a preformed slug, with up to several unit-sized slugs placed in the transfer pot to mold a larger-sized item.

Preheating, if practicable and controllable, may effectively reduce the required time for molding.

Molding. Mold temperatures vary between 270 and 400°F. Molding pressures up to 5000 psi are required and are usually determined by allowing 250 to 500 psi per inch of mold draw, or by predetermining plasticity of the compound.

The plasticity or "flow" of a molding compound is also very important in predetermining whether the compound will properly fill all extremities of the mold during the press cycle. ASTM Method D731 has been prepared to provide an index of this "flow" factor. ASTM molding indices of 2500 for extremely soft (high-flow) materials (660 psi minimum pressure required) to 20,000 for very hard (low-flow) materials (5260 minimum pressure required) are determined by measuring pressure necessary to close a standard cup mold to a specified finished thickness. In addition to composition, the "flow" of a molding compound depends also upon the age of the resin.

Shrinkage or difference between room-temperature dimensions of a mold and the article molded therefrom is another parameter governing successful molding, and is measurable by ASTM Method D955.

Rate of cure is an additional property requiring control, and information is generally supplied by the compound manufacturer (see Appendix II-2.4).

Special compounds require charging at a mold temperature of 170°F and subsequent increase to 350°F, with a 20 to 30-minute cycle. These are designed for superior elevated-temperature strength properties and ablation resistance.

Cold pressure molding to form a part, followed by oven curing, constitutes an original molding method still in use. Molded articles have poorer surface, lower impact, and higher water absorption than hot-molded articles, and are slightly lower in mechanical strength.

Common fillers and reinforcements for molding compounds are wood, nutshells, sisal, mica, clays, asbestos, graphite, nylon, rubber, glass,

Figure II-2.2. Acoustical ceiling panels made from phenolic-bonded compressed fiber-glass insulation board. (*Courtesy Johns-Manville Fiber Glass Division*)

and silica fibers.[6,27] A mold-release agent is also usually added when the mix is compounded.

A method has been outlined[6] for in-the-molding-shop preparation of a glass reinforced phenolic compound. It was intended for use on an equivalent basis with polyester premix material, and also yielded properties similar to a good-grade, high-reinforcement phenolic compound. Although having distinct advantages of cost saving and maximum possible raw-material inspection, the method has not to date gained wide commercial acceptance. This is probably due to the greater ease of handling an almost completely prepared compound in a molding plant.

Finishing. Small molded parts are sometimes tumbled together in a large drum for deflashing purposes. Larger parts are hand-finished.

Molded Properties.[28] ASTM Standard D796 discusses a method recommended for molding test specimens for determining physical and electrical properties of molded phenolic compound materials. ASTM D648 for heat deflection temperature is also applicable.

A comparison of the properties of basic types of molding compounds including phenolic and polyester premixes is presented in Table II-2.2.[4,6,28,29,30]

Table II-2.2. Comparative Properties of Molding Compounds

	General Purpose	Impact	Nonbleeding	Electrical Grade	Heat Resistant	Phenolic Premix	Polyester Premix
Flexural strength, psi*	11,000	20,000	10,000	10,000	9,500	8,500	15,000
Tensile strength, psi*	7,000	7,000	7,000	6,500	6,500	5,000	5,280
Tensile modulus, psi (×10⁶)	1.2	1.3	1.4	2.0	2.0	0.9	2.1
Compressive strength, psi*	30,000	16,400	22,000	25,000	22,000	19,000	28,900
Izod impact, ft lb/in.*	0.28	15	0.30	0.4	0.30	1.7	2.07
Heat deflection, 264 psi, °F	300	400	320	340	300 (450-short term)	275	—
Water absorption, 24 hr %	0.7	0.8	1.0	0.2	0.4	1.5	0.7
Specific Gravity	1.38	1.83	1.37	1.65	1.60	1.22	2.07
Dielectric strength, V/mil							
short term†	400	400	190	375	250	71	—
step-by-step†	300	300	190	350	270	—	—
Volume resistivity, ohm-cm (×10¹²)*	1	1	1	1	1	.0053	—
Dissipation (power) factor, 60 cycle*	0.07	0.05	0.15	0.16	0.08	—	—
Dielectric constant, 60 cycle*	5.2	6.8	10.8	10.3	7.0	—	—
Reinforcement or filler and approximate amount	Wood-flour	1-in. fiber glass roving 35–40%	Wood-flour	Mineral and flock	Mineral and wood flour	¼-in. sisal 15%	½-in. glass fiber—12.7
Curing properties or conditions	Fast + long flow	Low flow	Fast cure	Average cure	Fast cure	375° F 1600 psi	300°F 1000 psi
Special properties		Good chemical resistance	Odorless	Low shrink	Good molded surface		

* 48 hours at 50°C, tested at room temperature
† 48 hours at 50% R.H. at 23°C

Laminating

Phenolic resins for laminating are essentially the weak-base-catalyzed, one-step (resole) type, and are referred to as varnishes, probably due to the early attempts to supersede natural varnishes and lacquers with phenolics for the purpose of improving electrical properties.

Laminate types are either industrial or decorative. Phenolic laminate constructions are of two types: (1) multilayers of impregnated fibrous or other reinforcement sheets stacked and cured together, or (2) a sandwich construction composed of thin, laminated, high-strength facing sheets enclosing a thicker, low-density honeycomb or foam core.

The method of preparing laminates of the first type generally proceeds as follows:

(1) Reinforcement (paper or glass fabric) on rolls and under tension is impregnated by dipping into a liquid resin bath.

(2) Volatiles are removed and the resin cure is advanced by passing the impregnated sheet through a continuous drying oven. If required, cutting to size and stacking follow. However, at this stage, the fabric may be rerolled (interleaved) for later use as a prepreg material.

(3) Curing for 20 to 30 minutes in multiple-layer flat platen or other suitable equipment completes the cycle. Flow properties of the resin are measured by determining the percentage of resin which migrates from four stacked four-inch discs of the treated reinforcement molded in a test press for ten minutes at 300°F and 15 psi. The percentage of volatile material in the resin-impregnated cloth is also a useful parameter, and is determined by subjecting a weighed piece of the cloth to 320°F heat for ten minutes.

(4) The laminates *per se* may also be produced by a continuous extrusion or laminating process, in addition to the multiple-press operation.[31] Laminating temperatures range from 275 to 325°F. Pressure is induced by a series of rolls or by a continuous belt.

Sandwich-laminate construction (type 2) involves the sealing of two facing laminates together using appropriate core material (foam or honeycomb) and mastics to establish a desired thickness. Sandwich laminates are produced for purposes of combining high strength, rigidity, thermal, sound, or electrical insulation qualities with lightness of weight.

Laminates are ultimately machined, punched, drilled, or otherwise finished to create the desired end product.[32] (See Section VII).

Reinforcing materials for phenolic laminates include glass, silica, or asbestos or organic-fiber woven or nonwoven fabrics, kraft or cellulose paper, and also special refractory woven or nonwoven materials for use in applications where resistance to high temperatures is required. (See Section III).

In producing decorative laminates using phenolic-impregnated kraft paper as the "core-stock" material, either melamine-formaldehyde or urea-formaldehyde resin is used to impregnate both the decorative paper sheet (subsurface) and a clear cellulose paper reinforcement (top). These are necessary due to the tendency of the phenolic resin to darken upon curing. A phenolic resin modified to have appreciable plasticity at temperatures of 300 to 350°F makes possible postforming, in which flat-pressed laminates, especially the decorative type, may be given a rolled or curved leading edge, or otherwise made to serve an end-use requirement. A V-block test designed by NEMA (National Electrical Manufacturers Association) is useful in evaluating resins for potential use in postformable laminates.

A problem in postforming arises from the differential thermal expansion between the melamine or urea and the phenolic components of the laminate. Warpage or "cure" may be eliminated by holding the volatile content of the melamine print sheet low and that of the phenolic core stock high. The degrees of lowness and highness must be consistent with preparation of a satisfactory decorative laminate.[33]

The method for conducting the V-block test is outlined in NEMA Publication LP-2.[34] Also presented are methods of conducting tests desired to evaluate decorative laminates for surface wear, color fastness, mechanical strength, resistance to chemicals, boiling water and other performance requirements.

Industrial laminates made with phenolic resins are used primarily in electrical applications, although many other uses are extant, involving the innate low cost and good mechanical and chemical-resistant properties of the phenolic materials. Cellulose paper and nylon are used for the major part of the electrical laminates, some of which are copper-clad for printed circuitry. Cotton fabrics are desirable in preparing laminates which may be punched, machined into gears, etc., or threaded; and glass, asbestos, silica, or graphite fibers are employed for high-temperature-resistant laminates.[4,35]

Industrial laminate types and their respective properties are thoroughly described in the NEMA Standards LP-1, LI-3, 240.[34,36,37] Twenty-five distinct grades of industrial laminates are defined, and typical applications, forms into which end products may be fabricated, and minimum physical and electrical strength performance requirements are outlined. Epoxy, silicone, and melamine resins and vulcanized fiber are also included.

Production of void-free laminates has also been described,[1] with variables encountered in void-free structures being defined as: (a) the rate of release of volatile material from the resin; (b) the rate of decrease in resin viscosity due to the temperature increase (during molding); and (c) the rate of increase in viscosity due to the cure (polymerization) of the thermosetting resin.

Specific properties of phenolic-glass laminates may be determined by consulting references 12, 13, 14, 15, 16 and 17. Military Specification MIL-R-9299 outlines properties and performance requirements for phenolic low-pressure laminating resins. A comparison is made in

Table II-2.3 of physical properties of laminates made using a high-grade phenolic resin with those made using the "Standard" general-purpose rigid polyester.

TABLE II-2.3 TYPICAL PROPERTIES OF HIGH-GRADE PHENOLIC LAMINATING RESIN COMPARED TO THOSE FOR GENERAL-PURPOSE RIGID POLYESTER LAMINATE

	Phenolic Resin Vacuum-Bag Molded, 10-14 psi 181 Glass Cloth (Volan-A)	Phenolic Resin Laminated 1000 psi 181 Glass Cloth A-1100 Finish	G.P. Rigid Polyester 181 Glass Cloth 136 Finish
Flexural strength, psi (RT)	68,000	82,000	58,000
After ½ hr @ 600°F (tested at 600)	88,000	62,000	(Heat defl. = 293 F)
Flexural modulus, psi	3.4×10^6	4.0×10^6	3.0×10^6
Tensile strength, psi	48,000	48,000	45,000
Compressive strength, psi	37,000	60,000	35,400
Water absorption, %	3.5	0.10	0.13
Specific gravity	—	—	1.49
Resin content	25%	29%	38%

APPENDIX II-2.1—PHENOLIC RESIN TESTS[21]

TEST: FREE FORMALDEHYDE CONTENT OF PHENOLIC RESINS—HYDROXYLAMINE HYDROCHLORIDE METHOD

Applications of Test

1. This method is used to determine the free formaldehyde content of phenolic resins and formalin solutions to be used for the manufacture of phenolic resins.

Apparatus

2. a) Balance, accurate to 0.01 gram.
   b) Beaker, 400 ml.
   c) Buret, range 50 ml, graduated to 0.1 ml.
   d) Graduate, 100 ml, graduated to 1.0 ml.
   e) Magnetic stirrer.
   f) pH meter.
   g) Weighing bottle.

Reagents

3. a) 2B alcohol.
   b) Aqueous hydroxylamine hydrochloride solution, 10%.
   c) 1*N* standard sodium hydroxide solution.
   d) 0.1 *N* sulfuric acid solution.

Procedure

4.0 Water-soluble resins
   a) Weigh a 400-ml beaker to the nearest 0.01 gram (or tare with lead shot).
   b) Weigh into the beaker 10 grams of sample to the nearest 0.01 gram, and dissolve in 150 ml of distilled water.
   c) Neutralize to a pH of 4, using the pH meter, and 0.1*N* sulfuric acid solution while stirring.
   d) Add 40 ml of hydroxylamine hydrochloride solution.
   e) Wait 5 minutes for a process sample and 20 minutes for a final sample, then titrate with 1*N* sodium hydroxide solution to a pH of 4.0. Record the titre. If more than 45 ml of titre is used, reduce the sample size and repeat the above procedure.

4.1 Phenolic Varnishes
   a) Weigh a 400-ml beaker to the nearest 0.01 gram.
   b) Weigh into the beaker 10 grams of sample, to the nearest 0.01 gram, and dissolve in 125 ml of 2B alcohol and 25 ml of water.
   c) Follow the procedure in Section 4.0, steps (c) through (e).

4.2 Feedmix-All phenolic resins
   a) Measure 150 ml of distilled water into a 400-ml beaker.
   b) Weigh 2.00 ± 0.01 grams of sample into the beaker, by difference.
   c) Dissolve by placing on a magnetic stirrer.
   d) Follow the procedure in Section 4.0, steps (c) through (e).

4.3 Blank titre
   a) Determine the blank titre on 40 ml of hydroxylamine hydrochloride solution by titrating to a pH of 4.0 with standard sodium hydroxide solution. For feedmix blank titre, add 150 ml of water to the hydroxylamine hydrochloride.

Calculation

5. Formaldehyde, per cent by wt.

$$= \frac{(\text{ml titre} - \text{ml blank titre}) \times \text{normality} \times 3.003}{\text{Wt. of sample}}$$

Report

6. Report the per cent formaldehyde to the nearest 0.1%.

APPENDIX II-2.2—PHENOLIC RESIN TESTS

TEST: NONVOLATILE MATTER ("METHANOL SOLIDS") IN WATER-SOLUBLE PHENOLIC RESINS

Applications of Test

1. This method is used to determine the quantity of nonvolatile matter present in water-soluble phenolic resin solutions under arbitrary test conditions. Methanol is used as a drying aid unless otherwise specified.

Apparatus

2. a) Thermometer, range 0–200°C, graduated to 1°C.
   b) Oven, gravity convection type, controlled to 150°C ± 1°C.
   c) Stoppered weighing bottle.
   d) Drying dishes, seamless tin with metal cover, having an inside diameter of approximately 2⅛ in. and a height of approximately 1⅛ in.
   e) Desiccator.
   f) Balance, accurate to 0.0001 gram.

Reagents

3. a) Methanol, reagent grade, acetone-free.
   b) Anhydrous ethanol.
   c) 2B alcohol.

Procedure

4. a) Heat 3 drying dishes for at least *30 minutes* in the 150°C oven. Cool for at least *15 minutes* in a desiccator. Mark each dish in some manner for identification and weigh to the nearest 0.0001 gram. Pipette 10 ml. of methanol, unless otherwise specified on batch analysis sheet, into each dish. From the stoppered weighing bottle, weigh by difference to the nearest 0.0001 gram 1.9 to 2.1 gram of the resin solution into each drying dish.
   b) Dissolve the resin solution by a slight circular motion. Touch the pan bottom lightly to a hot plate and swirl if difficulty is encountered in dissolving the resin. Place covers in a tilted position on the dishes such as to permit evaporation but to prevent loss by spattering.
   c) Within *30 minutes* after preparation, place the partially covered drying dishes in the constant-temperature oven (Note 7a), in close proximity to the bulb of the thermometer, and allow them to remain for a period of *2 hours ± 5 minutes*. (Note 7b).
   d) At the end of the 2-hour heating period, remove the dishes to the desiccator and cool for *15 to 20 minutes* at room temperature. Then weigh the drying dishes with the residues immediately to the nearest 0.0001 gram.

Calculations

5. Nonvolatile matter, per cent

$$= \frac{\text{wt. of residue}}{\text{wt. of sample}} \times 100.$$

Report

6. Report per cent nonvolatile matter to the nearest 0.01% "methanol solids." List all three results.

Notes

7. a) In a gravity-type oven, which depends upon the natural circulation of air for uniformity of temperature, use only one shelf for supporting the specimens. Check all vents of the oven to be sure they are open.
   b) Place only one set of solids in the oven at any given time. Solid sets may be inserted at 1-hour intervals, if necessary.

APPENDIX II-2.3—PHENOLIC RESIN TESTS

TEST: NONVOLATILE MATTER IN VARNISH PHENOLIC RESINS

Application of Test

1. This method is used to determine the nonvolatile content of phenolic varnishes, based on an arbitrary set of conditions.

Apparatus

2. a) Balance, accurate to 0.0001 gram.
   b) Drying dishes, seamless tin, having an inside diameter of approximately 2¾ inches and a height of approximately $^5/_{16}$ inches. A standard pint tin can cover is suitable for this use.
   c) Desiccator.
   d) Oven, gravity connection, controlled at 135°C ± 1°C.
   e) Weighing bottle and stopper.
   f) Thermometer, range of 0 to 200°C, graduated to 1°C.

Procedure

3. a) Heat 3 drying dishes for at least *30 minutes* in the 135°C oven. Cool for at least *15 minutes* in a desiccator. Mark each dish in some manner for identification, and weigh to the nearest 0.0001 gram. From the stoppered weighing bottle, weigh by difference to the nearest 0.0001 gram, 1.4 to 1.6 gram of the resin solution into each drying dish. Spread the resin sample over the bottom of the drying dish evenly. Use a slight tilting circular motion to facilitate even spreading.
   b) Within *30 minutes* after preparation, place the drying dishes in the constant-temperature oven, in close proximity to the bulb of the thermometer, and allow them to remain for a period of *3 hours ± 5 minutes*.
   c) At the end of the 3-hour heating period, remove the dishes and place them in the desiccator for *15 to 20 minutes*. Then weigh the drying dishes with the residues immediately to the nearest 0.0001 gram.

Calculation

4. Nonvolatile matter,

$$\% = \frac{(\text{wt. of residue + dish}) - (\text{wt. of dish})}{\text{wt. of sample}} \times 100$$

Report

5. Report the average of the three determinations to the nearest 0.01%. Do not use results more than 0.8% apart. At least two results are to be used in the report.

APPENDIX II-2.4—PHENOLIC RESIN TESTS

TEST: DILUTABILITY OF WATER-SOLUBLE PHENOLIC RESINS—STANDARD METHOD

Applications of Test

1. This test is used to determine the tolerance of water-soluble phenolic resins for water, *without* producing turbidity.

Apparatus

2. a) Beaker, 600 ml.
   b) Graduate, range 250 ml, with glass stopper, graduated to 2 ml.
   c) Graduate, range 10 ml, graduated to 0.5 ml.
   d) Constant temperature bath, controlled at 25°C ± 0.5°C.

Procedure

3. a) Fill a 600-ml beaker with water and maintain this water at a temperature of 25°C ± 0.5°C (Note 6). Cool the sample to 25°C ± 0.5°C. Using a 10-ml graduate, transfer 10.0 ml of the sample to a 250-ml graduate. Add 10.0 ml of the 25°C water to the same small graduate used for the sample. Shake well and transfer the contents to the 250-ml graduate. Repeat this procedure twice. Mix resin and water in the 250-ml graduate by tilting the stoppered graduate back and forth until the solution is uniform. If the solution is transparent, add an additional 10.0 ml of water and mix as before. Continue the addition of water in 10.0 ml increments, mixing with the solution and always maintaining the temperature of the mixture at 25°C ± 0.5°C until the solution is distinctly turbid (Note 5). Record the dilution at which turbidity is first observed.
   b) In some cases, the method results in only a faint or indistinct turbidity, and the turbidity does not increase sharply upon further additions of water. Record this fact and the dilution at which faint turbidity is first observed.

Calculation

4. Per cent dilutability

$$= \frac{(\text{total ml water and sample}) - 20}{10} \times 100$$

Report

5. a) Report the per cent dilutability to the nearest hundred.
   b) A dilutability of over 2400% is reported as infinity.
   c) If a faint turbidity should appear at one point of the dilution test without sharply increasing upon further addition of water, this fact must be reported in the results.

Notes

6. Since the water dilutability of water-soluble resin is greatly affected by the temperature of the test, the required temperature of 25°C ± 0.5°C should be strictly adhered to.

APPENDIX II-2.5—PHENOLIC RESIN TESTS

TEST: STROKE CURE OF PHENOLIC RESINS, HOT-PLATE METHOD

Application of Test

1. This method is used to determine the curing time of thermosetting resins.

Apparatus

2. a) Deflagration spoon, bowl ¼-inch deep and ¾-inch in diameter.
   b) Emery cloth, No. 0.
   c) Hot plate, 6 inch x 6 inch surface controlled at 150 ± 0.5°C.
   d) Montan wax or substitute.
   e) Thermometer, range 0 to 200°C, graduated to 1°C.
   f) Spatula, metal, 4 inch.
   g) Timer, accurate to 1 second.

Procedure

3. a) Set up the hot plate in an area shielded from drafts.
   b) Coat the hot plate with a thin film of montan wax. Wipe off any excess that may occur. The wax will make removal of the cured resin easier after the test is completed.
   c) Adjust the hot plate to 150 ± 0.5°C. Stir the resin thoroughly and, using the deflagration spoon, place a single spoonful of resin in the center of the hot plate. At the same time, start the stopwatch and spread the resin with a circular motion of the spatula. *Use only enough pressure to bring the spatula into a flat position on the hot plate.* Gradually spread the resin over an area about five inches in diameter. If the resin pulls up on the top of the spatula, do not try to return it to the plate surface. It may be scraped off on an edge of the hot plate if necessary.
   d) Stop the stopwatch and record as the cure point the time at which the material ceases to bridge or stretch when the spatula is raised from the hot plate surface. When the spatula is slid across a cured resin the resin either "rolls" or else offers very little resistance to the spatula's motion.
   e) Check the temperature to make sure it has not changed during the test.
   f) At least two checks agreeing within a range of ± 5% from the average of both tests should be made.
   g) Clean the hot plate by scraping with the *brass* spatula and polish with emery cloth, if necessary, immediately after completion of the test. The quicker the resin is removed from the surface, the easier the task will be. If the surface is not clean, erroneous cure times will result.

Report

4. Report the time to cure in seconds and the test temperature in degrees centigrade.

APPENDIX II-2.6—PHENOLIC RESIN TESTS

TEST: SET TIME OF PHENOLIC VARNISHES

Applications of Test

1. This method is used to determine the relative rate of polymerization of varnishes at a given temperature.

Apparatus

2. a) Agitator, a 12-inch length of 5-mm glass rod sealed to a 5-cm length of 9-mm glass rod.
   b) Balance, accurate to 0.01 gram.
   c) Constant temperature bath, controlled at 135°C ± 1°C.
   d) Laboratory motor, 350 rpm, with chuck to fit 9-mm rod.
   e) Test tubes, Pyrex, 150 mm × 20 mm.
   f) Test tube clamp.
   g) Timer, accurate to 0.1 second.

Procedure

3. a) Attach the glass-rod agitator to the bottom of the laboratory motor. Weigh, to the nearest 0.1 gram, 2.4 to 2.6 gm of the resin sample into a test tube. Slip the mounted agitator rod into the test tube. Lift the test tube up until the agitator touches the test tube bottom lightly. Center the agitator in the test tube, then clamp the test tube into this position tightly.
   b) Lift the motor-agitator-test tube assembly and swing it over the constant-temperature bath. Lower the assembly into the bath and immediately start both the laboratory motor and the timer. Stop the timer when the material under test transfers to the agitator and covers the enlarged portion completely (see Note 5). This endpoint is also indicated by a change in the resin from a brown liquid to an amber, gel-like solid. Another indication that the endpoint is reached is when the agitator rotates in a noisy, wobbly fashion. A warning that the end point is near occurs when the bubbles being formed no longer rise rapidly but are "stretched out" and spiral slowly upward in the liquid.

Report

4. Report the time in seconds, as "set time."

Notes

5. In some cases, transfer of the resin to the agitator is not complete. The change from liquid to an amber, gel-like solid and the wobbling agitator still hold true and are the best means to detect the end point.

References

No.	Author(s)	Title or Periodical	Vol.	P.-Sect.	Year
1	Kline, G. M., ed.	Analytical Chemistry of Polymers, Part I, New York Interscience Publishers, Inc.	—	227	1959
2	Bjorksten, J.	Polyesters and Their Applications, New York, Reinhold Publishing Corp.	—	104	1956
3	Hatch, D. M., Jr.	"Development of Fabrication Technique for High-Temperature Resistant Structural Compounds," SPI-R.P. Div. Preprint	8	34	1953
4	White, R. B.	"Glass Premix Molding;" SPI-R.P. Div. Preprint	9	110	1954
5	Morgan, P. A.	Glass Reinforced Plastics; Iliffe, 2nd Ed.	—	—	1957
6	Shand, E. B.	Glass Engineering Handbook; New York, McGraw-Hill Book Co., Inc.	—	—	1955

No.	Author(s)	Title or Periodical	Vol.	P.-Sect.	Year
7	Bartel, E. H. Landry, R. J.	"Calorobic Plastics for Use in Rocket Motors;" SPI-R.P. Div. Preprint	10	10E	1961
8	Colao, J. J.	"Comparison Phenolic and Polyester Premix Materials;" SPI-R.P. Div. Preprint	13	9A	1958
9	Gould, D. F.	"Phenolic Resins," New York, Reinhold Publishing Corp.	—	—	1959
10	Anon.	NEMA Standard LP-1 for Industrial Laminated Thermosetting Products	May	—	1950
11	Anon.	NEMA Standard LP-2 for Laminated Thermosetting Decorative Sheets	May	—	1957
12	Anon.	Technical Bulletin, Taylor Fibre Co.	—	—	1961
13	Boller, K. H.	"Fatigue Properties of Various Glass-Fiber Reinforced Plastic Laminates," WADC Tech Report No. 55-389	—	—	1956
14	Werren, F. Heebink, B. G.	"Weathering of Glass-Fabric-Base Plastic Laminates," WADC Tech. Report No. 55-319.	—	—	1956
15	O'Brien, F. R. Oglesby, S., Jr.	"Investigation of Thermal Properties of Plastic Laminates, Cores and Sandwich Panels," WADC Tech Report No. 54-306, Part 1 & 2.	—	—	1955
16	Gynn, G. M. Vanecho, J. A. Simmons, W. F.	"Elevated and Room Temperature Properties of Conolon 506 Plastic-Glass Fabric Laminate;" WADC Tech Report No. 57-574	—	—	1957
17	Anon.	"Plastics for Flight Vehicles," ANC-17 U.S. Forest Products Lab.	—	—	1958
18	Anon.	Modern Plastics Encyclopedia Issue	37	128	1960
see also	Landall, A. P. Lidstone, J. B.	Modern Plastics Encyclopedia Issue	38	246	1961
see also	Anon.	Modern Plastics Encyclopedia Issue	39	228	1962
19	Golding, B.	Polymers and Resins, D. Van Nostrand Co., Inc.	—	242	1959
20	Davies, A.	Personal Communication (Allied Chemical Corp).	—	—	Feb. 21, 1962
21	McGill, L.	Personal Communication (Allied Chemical Corp.)	—	—	Mar. 1, 1962
22	Anon.	Technical Data Notebook, Durez Plastics Div., Hooker Chemical Corp.	—	—	—
23	Anon.	Technical Data Bulletins, Fiberite Corp.	—	—	—

No.	Author(s)	Title or Periodical	Vol.	P.-Sect.	Year
24	Anon.	"Recommended Practice for Fabricating Laminated Plastics," NEMA Publication No. 45-107 (out of print)	—	—	Dec., 1945
25	Erickson, W. O. Ahrberg, W. R.	"Study of Various Reinforcing Materials in Polyester Premix Compounds;" SPI-R.P. Div. Preprint	12	17-C	1957
26	Susman, S. E.	"A High-Temperature Structural Adhesive," SPI-R.P. Div. Preprint	9	7-I	1954
27	Caron, P. E. Lydis, L. L.	"Pres-Tock—A New Material for Compression Molding," SPI-R.P. Div. Preprint	17	3-D	1962
28	Anon.	"High-Temperature Properties of Industrial Thermosetting Laminates," NEMA Standards Publication L13	Aug.	—	1961
29	Anon.	"Test for Flame Resistance of Laminated Sheets or Cast Insulating Materials," NEMA Standard Publication No. 240	Mar.	—	1961
30	Skeist, I.	"Survey of Recent Advances in Resins for Reinforced Plastics," SPI-R.P. Div. Preprint	12	15-A	1957
31	Morris, W.	"A Study of Curl in Decorative Laminates," TAPPI	42 #7	—	July, 1959
32	Hannes, G. J.	Personal Communication (Johns-Manville Fiber Glass Div.)	—	—	Mar. 28, 1962
33	Latham, M. E.	"Low-Pressure Decorative Laminate," SPI-R.P. Div. Preprint	15	2B	1960

Chapter II-3

EPOXY RESINS

INTRODUCTION AND DEFINITIONS

Epoxy resins are characterized by the presence of oxirane or epoxide groupings

$$-\underbrace{C-O-C}-$$

These may be present in the raw materials reacted to form the resin (conventional or novalak types) or may be formed during the reaction (epoxidized polyolefinic type). Reactive hydroxyl groups and vinyl unsaturation also appear in specific epoxy resin molecules.[8]

Whichever the case, aromatic or aliphatic polymer molecules containing an average of more than one of the epoxide groups comprise epoxy resins.[7] The groups may occupy various attitudes within the molecule, such as terminal, internal, ring situated, glycidyl, etc.

Cure may be established using materials classed as hardeners or curing agents. These react to polymerize epoxy resins through either one of two methods: (a) catalytic means in which the epoxide groups on the resin molecules interact (catalytic example—boron trifluoride), or (b) by cross-linking, in which copolymerizing molecules unite with the epoxy resin molecules becoming part of the cured resin network (example—amine curing agents).[6,7] In both cases, the epoxide groups are opened, and subsequently a well-knit polymer structure is formed. The three-membered epoxide ring is of interest due to its high reactivity potential, contributing to the fact that epoxy resins *per se* have exhibited interesting and superior cured properties. This is true primarily because, during cure, no rearrangement occurs in the backbone of the resin molecule, the reactive epoxide groups actually being held on the uncured molecule as appendages.

Table II-3.1 presents a classified summary of the three major types of epoxy resins of commercial significance: (a) epichlorhydrin-bisphenol A (conventional), (b) epoxy novolak, and (c) epoxidized polyolefin resins. Curing agent or hardener systems for the conventional epoxies are described and their properties and optimum reaction quantities summarized in Table II-3.2. Curing agents for the novolak and polyolefin epoxies are summarized in Table II-3.1.

The behavior and handling of epoxy resins will be clarified by noting the following definitions:

Epoxide Equivalent represents the accepted method of expressing epoxy resin functionality, and is the weight in grams of the amount of resin which contains one gram-chemical equivalent of epoxy (usually determined by HCl reaction and titration, and supplied by the resin manufacturer). *Epoxy Value* is another expression of epoxy resin functionality, and is defined as the number of epoxy groups contained in 100 grams of resin. Epoxy value is equal to the epoxide equivalent divided into 100. In order to determine required resin and curing-agent combining quantities, the *amine equivalent* is first determined by:

$$\frac{\text{Molecular weight of the amine curing agent}}{\text{Number of reactive hydrogen atoms in the amine molecule}}. \quad (1)$$

The required amount of curing agent (X phr) is then determined by equating the ratio of:

$$\frac{\text{epoxide equivalent}}{\text{amine equivalent}} \text{ to } \frac{100}{(X \text{ phr})} \quad (2)$$

As an example, diethylene triamine, $H_2N-H_4C_2-NH-C_2H_4-NH_2$, has a molecular weight of 103.2 and five reactive hydrogens are contained in the molecule, thus providing an amine equivalent of 103.2/5, or 20.7. Then, for a

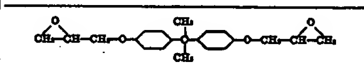
Text continued on p. 78.

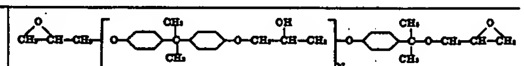
TABLE II-3.1. CLASSIFICATION OF COMMERCIALLY SIGNIFICANT EPOXY RESIN TYPES

	Conventional Epoxy Resins[39, 40]		Epoxy Novolak Resin[40]	Epoxidized Polyolefin[4, 5, 41]
1. *Chemical composition and/or classification*	Diglycidyl ether of bisphenol A with only smaller amounts of higher mol. wt homologs	High mol. wt homologs of diglycidyl ether of bisphenol A		
2. *Organic raw materials*	Bisphenol A, epichlorhydrin	Bisphenol A, epichlorhydrin, sodium orthosilicate	Novolak resin, epichlorhydrin	Olefin plus peracetic acid
3. *Mole ratios*	Actual (used in making resin) 1 (bis) to 4 (epi)[32] Theoretical (in cured resin) 1 (bis) to 2 (epi)	Theoretical Bis:Epi = Epoxide Equivalent 1.33 - 1 = 730 (approx) 1.25 - 1 = 862 (approx) 1.2 - 1 = 1176 (approx)	Moles[40, 41] Phenol / Moles Form. / M.W. of Novolak / Epoxy Novolak Functionality / Epoxide Equivalent a. 10 / 1 / 212 / 2 / 176 b. 10 / 3 / 300 / 2.6 / 179 c. 10 / 7 / 640 / 5.0 / 200	Typical Example[41] (Patented) 300 pts. polybutadiene in 300 pts. toluene 57 pts. glacial acetic acid 51 pts. sulfonic acid type cation exchange resin 146 pts. hydrogen peroxide
4. *Reaction catalyst*	NaOH (2 moles/mole bisphenol A) or other catalysts used to neutralize the HCl which is formed.	Excess NaOH used: 1.3 moles NaOH to 1.1 mols epichlorhydrin; other catalysts also used.	—	Ion-exchange resin
5. *Reaction procedure*	Bisphenol A and epichlorhydrin solution are stirred together at 100°C (approx) in N_2 atmosphere; NaOH solution added at slow rate to keep solution neutral; the organic layer (product) is separated, dried with sodium sulfate and vacuum distilled.[33]	Bis-A and Epi, sodium orthosilicate and NaOH solution are reacted at approximately 115°C and 25 psi for 30 minutes; viscous resin (product) is then water-washed under heat and pressure to remove caustic and salt; final water removed by heating, and hot resin poured from kettle and allowed to cool.	Resins of this type are prepared by reacting a phenolic-type novolak resin with epichlorhydrin under conditions somewhat similar to those used for conventional epoxy resins.	A polyolefin such as butadiene is first polymerized and then reacted with peracetic acid to produce the epoxidized polyolefin plus acetic acid. The peracetic acid may be either formed in situ or generated externally and added to the batch.
6. *Reaction type*	Dehydrohalogenation	Dehydrohalogenation	Dehydrohalogenation	Peracetic acid epoxidation
7. *Form of reacted resin*	Liquid	Solid	3-a Liquid (16 poise @ 100°F.); 3-b Liquid (210 poise @ 100°F.); 3-c Semisolid	Liquid
8. *Uncured resin properties:* Color Viscosity Specific gravity Epoxide equivalent Solubility Melting point Uncatalyzed stability	 Light yellow 100-160 poise @ 77°F Approx. 1.16 185-200 Most all organic solvents — One year	 Yellowish — — 400-5500 Ketones, alcohols, aromatic hydrocarbons Room temperature to 320°F One year	 — — 1.18-1.20 200-215 Ketones, aromatic hydrocarbons — One year	 Light yellow 1800 to 2300 poise at 77°F 1.0 (approx) 145-833 Ketones, aliphatic and aromatic hydrocarbons — One year

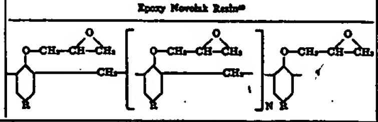
9. *Approximate chemical formula of resin*

Conventional Epoxy Resins[39, 40]

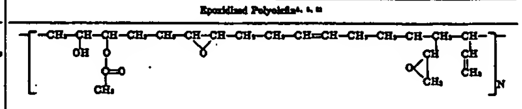




Epoxy Novolak Resin[40]



Epoxidized Polyolefin[4, 5, 41]



	Conventional Epoxy Resins[39, 40]		Epoxy Novolak Resin[40]	Epoxidized Polyolefin[4, 5, 41]
10. *Distinctive characteristics*	Comprises 85% of all epoxy resins used; least expensive among all epoxies.	Same	Greater degree of cross-linking than for conventional epoxies; therefore, novolaks have higher heat-deflection temperatures and better chemical resistance.	Contains reactive double bonds permitting cure in presence of vinyl-type monomers using peroxide catalysts plus anhydrides. The resins possess lower densities (1.00).
11. *Curing agents*	See Table II-3.2 for conventional epoxy resin curing agents	Same	Curing agents include metaphenylene diamine (11-13 PHR); dicyandiamide; phthalic anh. (40 PHR); chlorendic anhydride (114 PHR); PMDA-MA mixtures (13:23 PHR); and BF_3-MEA complex; optimum = nadic methyl anhydride + α-methyl benzyldimethylamine (80 + 1.5 PHR): cure = 30 min. at 374°F.; type 3-c (semi-solid) requires no B-staging.	Curing agents for the epoxidized polyolefin type are predominantly anhydrides and acids such as fumaric, hexahydrophthalic, chlorendic, maleic, pyromellitic dianhydride (room temperature cure), p-amino benzoic acid (prepreg). Typical system: fumaric acid—25PHR, dicumyl peroxide—1.5PHR, styrene—16PHR; cure 5 minutes at 300°F; HDT—518°F. Also useful are polyamines and phenolics (as resins).
12. *Typical uses*	Wet lay-up and prepreg laminates; filament winding; encapsulation, casting, potting, tooling, adhesives, paints and coatings. May be made flexible (long-chain additives, inert plasticizers, or special hardeners) and may be made self-extinguishing (bromine types).	Fluidized bed and flocked coatings, prepreg.	High-temperature structural and ablative laminates (lay-up, prepreg and filament-wound); also encapsulation, casting, tooling, adhesives, etc.; high-temperature resistance directly proportional to resin functionality.	Filament winding, laminates, molding compounds; 20% added to a G.P. polyester forms a resin alloy with improved properties at lower price than pure epoxy.

TABLE II-8.2. CURING AGENTS FOR CONVENTIONAL TYPE EPOXY RESINS

Type of Hardener	Typical Curing Agent Properties	Characteristics of Resin—C. A. System	Material	Examples: PHR for Optimum Heat Deflection Temp.	Examples: RT Pot Life* or Cure Time & Temp.	Examples: Heat Deflection Temperature (after full postcure) (°F)
1. Primary aliphatic polyamines[21, 22]	Low-viscosity liquids; disagreeable odor; irritating vapor; skin sensitizers.	Promote rapid cure at R. T., with short pot life and high exotherm; postcuring increases heat-deflection temperature; improves chemical resistance and electrical properties.	Diethylene triamine	12	29 min	248
			Triethylene tetramine	12	30 min	248
			Diethylaminopropylamine	8	RT (6 hr not cured) Cure: 2 hrs—250°F	216
			Dimethylaminopropylamine	4	Gel: 6 hr Cure: 2 hrs—250°F	248
2. Modified primary aliphatic polyamines	Liquids with viscosities similar to conventional resins; odor less noxious than No. 1; lower skin-sensitizing potential than No. 1.	Provide more convenient mixing ratios; faster curing, somewhat lower irritation potential; lower vapor pressure; tend to reduce physical & chemical properties.	Amine resin adduct	24	22 min	157
			Amine ethylene oxide adduct	20	18 min	194
			Cyanoethylation product	22.5	42 min	189
			Amine phenol (proprietary mixture)	16.5	11 min	223
3. Cyclic aliphatic amines	Low-viscosity liquids; vary from mild to strong vapors.	Long pot life; low exotherm possible; postcure usually required.	Piperidene	10	Thick gel: 2-6 hr Set: 32-48 hr	163
			N-aminoethyl piperazine	18	18 min	233
4. Aromatic amines	Solids (some proprietary aromatic amines are liquids); irritating vapor.	Higher heat deflection temperatures than aliphatic amines; can be used for B-staging.	Metaphenylene diamine[22]	21	6-16 hr	287
			Diamino diphenyl sulfone[23]	30	Cure: 1 hr-300°F	347
			Dicyandiamide (with solid resins)	4	Cure: ½ hr-345°F	—
5. Tertiary amines	Low-viscosity liquids; mild odor; low skin-sensitizing potential.	Long pot lives; can be used as accelerators for polyamide and anhydride cures.	Dimethylamino ethanol	4	Thick gel: 4-6 hr Set: 6-16 hr	234
			Benzyldimethylamine	9	Thick gel: 6 hr Set: 6-16 hr	186
6. Latent curing agents	Liquids and solids.	Long pot lives; cure activated by heat.	Boron trifluoride-monoethylamine complex	2-4	7 to 30 days Cure: 1 hr—250°F	338
			Triethanolamine borate	—	—	—
7. Polyamides[26, 27]	Medium to high-viscosity liquids; mild odor; low skin-sensitizing potential.	Impart flexibility to resins when cured.	Reaction product of ethylene diamine and the dimer of linoleic acid	64	100 min	220
8. Acid anhydrides[19, 23, 24]	Solids or liquids; corrosive and some are lachrymatory, but have low skin-sensitizing potential.	High heat-deflection temperatures; high-temperature resistance; superior electrical properties; require elevated temperature cures.	Phthalic anh.	40-60	Cure: 8 hr—300°F	190
			Maleic anh.	—	—	—
			Dodecylsuccinic anh.	120-150	Cure: 6 hr—200°F	158
			Chlorendic anh.	100-120	Cure: 2 hr—320°F	356
			Pyromellitic dianhydride[25] and Maleic anh. mixtures	PMDA-(13-21) to MA-(19-27)	Cure: 24 hr—320°F	392-500
			Hexahydrophthalic anh.	—	—	—
			Nadic methyl anh.	90	Cure: 2.8 hr—225°F	424

* Room temperature pot lives given for 100-gm epoxy resin plus hardener; epoxide equivalent of resin = 198.